Quinone electrochemistry in acidic and alkaline solutions and its application in large scale energy storage

Quinone electrochemistry in acidic and alkaline solutions

& its application in large scale energy storage

Michael R. Gerhardt[1], Kaixiang Lin[2], Qing Chen[1], Michael P. Marshak[1,3], Liuchuan Tong[2], Roy G. Gordon[1,2], Michael J. Aziz[1]

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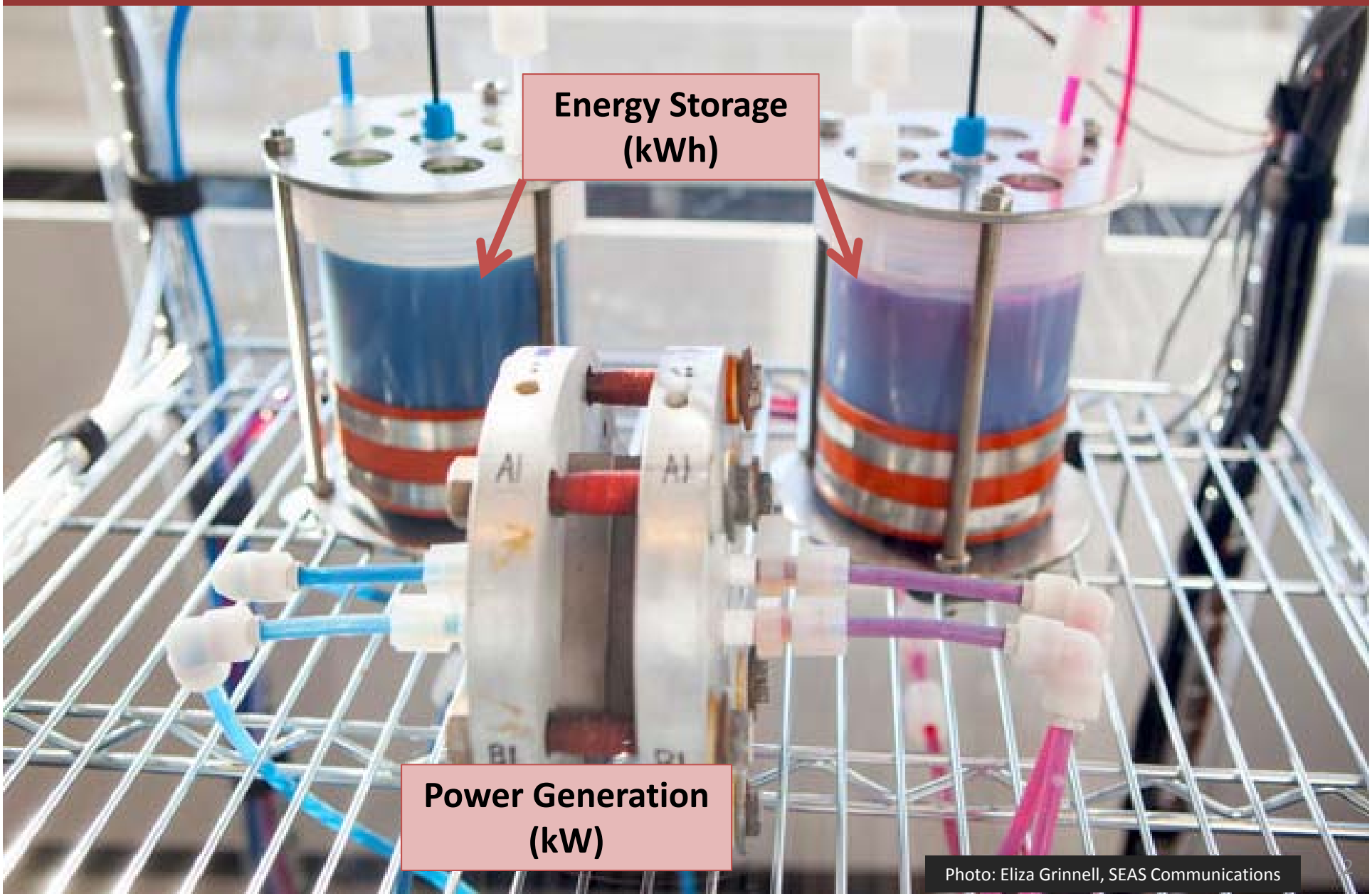
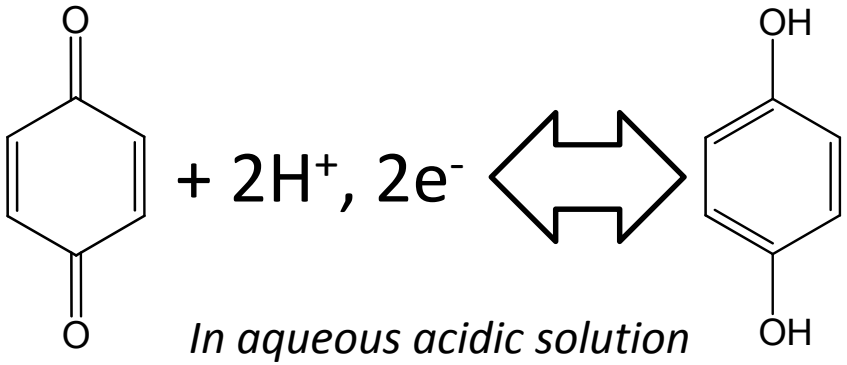
2) Department of Chemistry and Chemical Biology, Harvard University, Cambridge MA 02138

3) Department of Chemistry and Biochemistry, University of Colorado, Boulder CO 80309

Flow Batteries Store Energy



Quinones are Cheap, Versatile, & Robust



In aqueous acidic solution

Huskinson, B., Marshak, M. P., Suh, C., Er, S., Gerhardt, M.R., Galvin, C.J., Chen, X., Aspuru-Guzik, A., Gordon, R.G., and Aziz, M.J. (2014). *Nature*, *505*(7482), 195–198.

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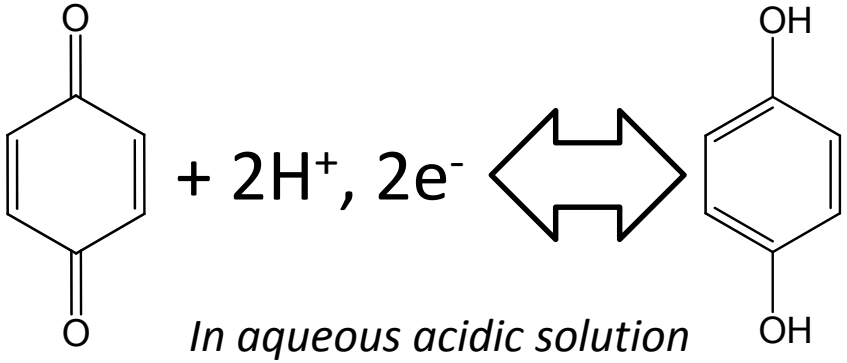

In aqueous acidic solution

Chemistry	Solution Cost ($/kWh)
Quinone-Bromide	<$27
Vanadium Redox	$50 – $180

"I wish I could get that price!"

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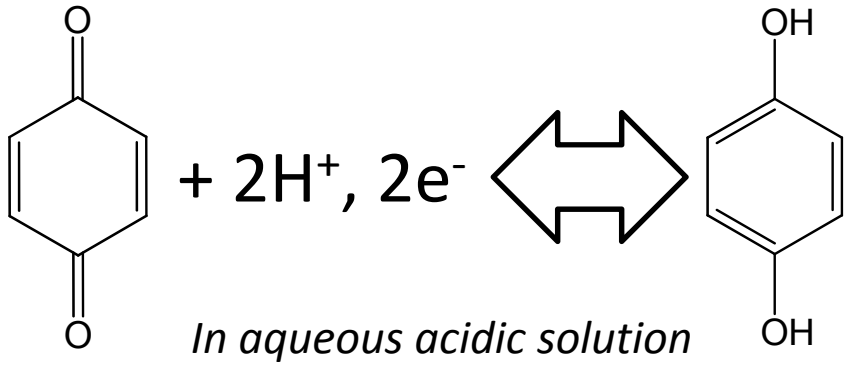

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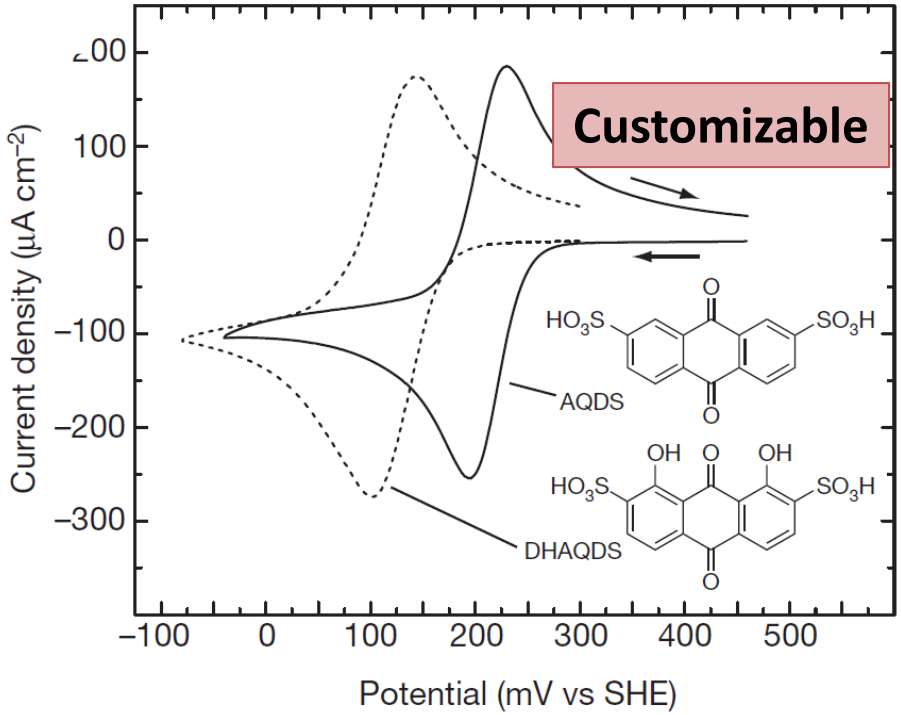

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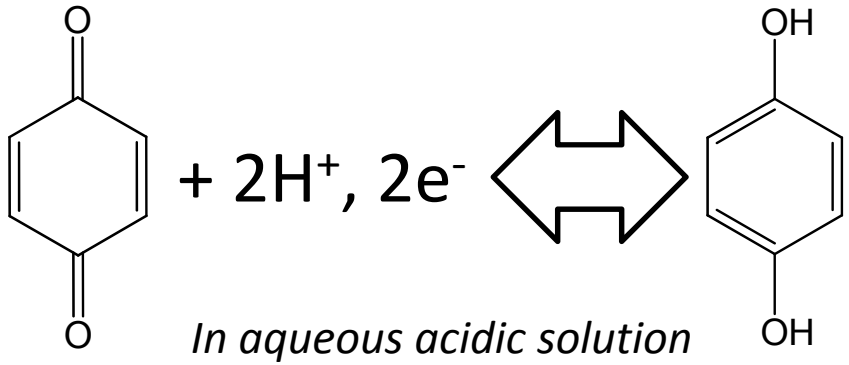

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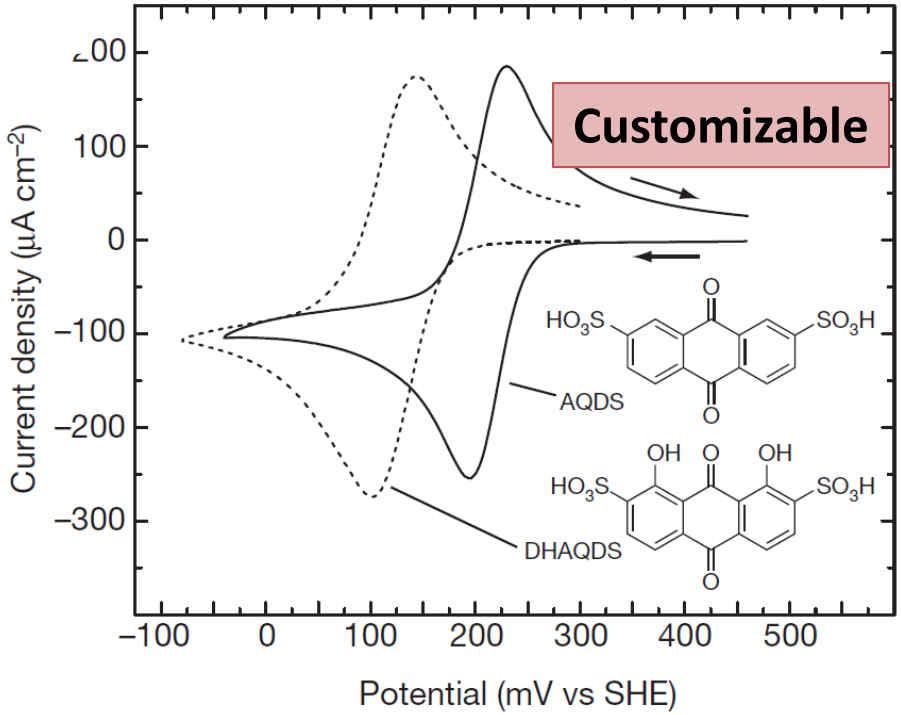

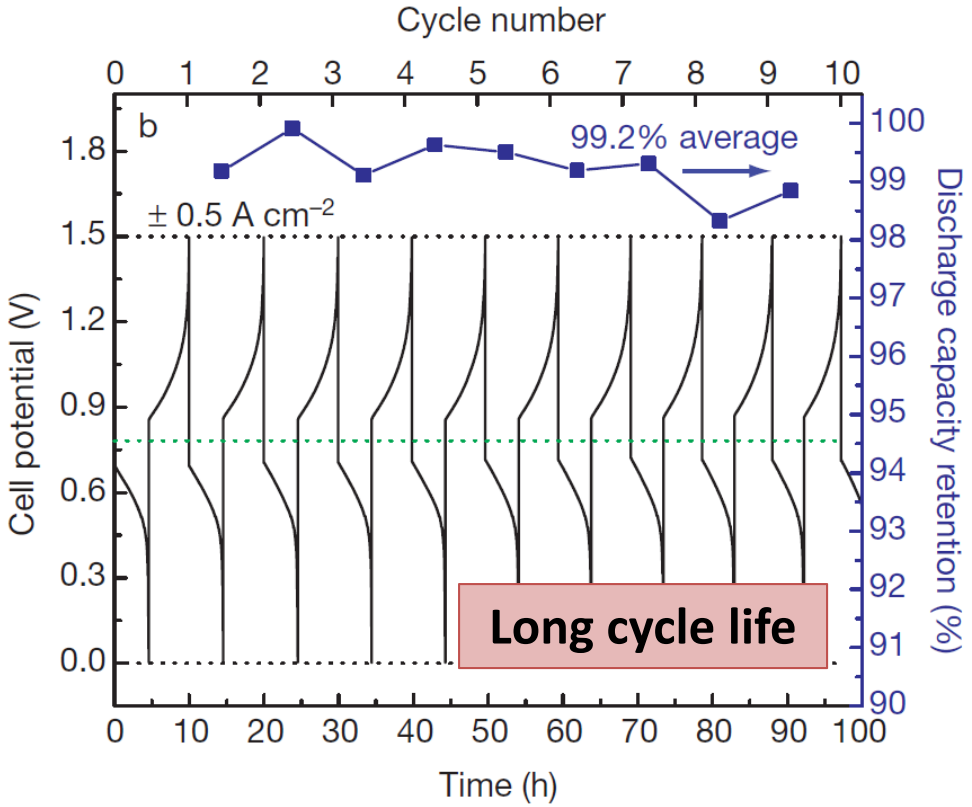

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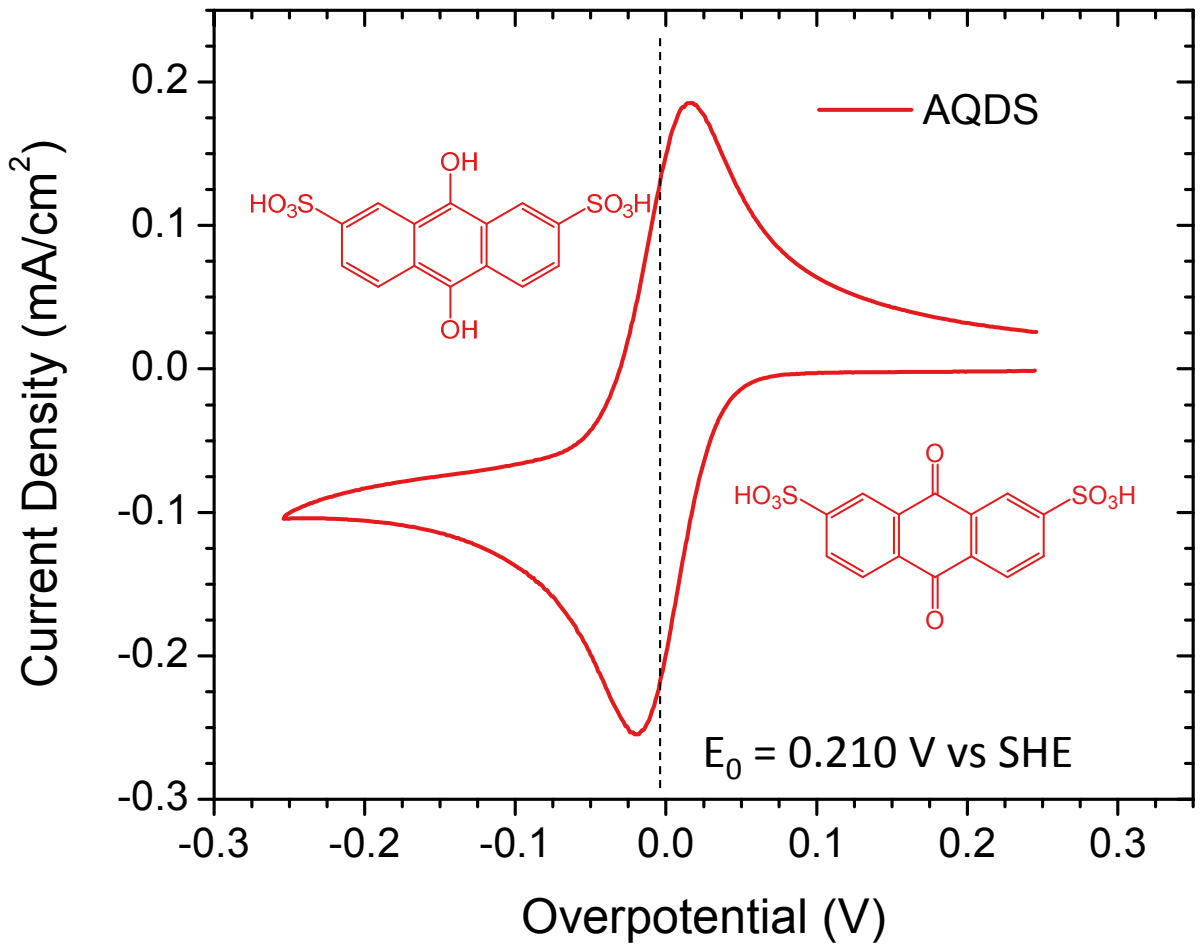
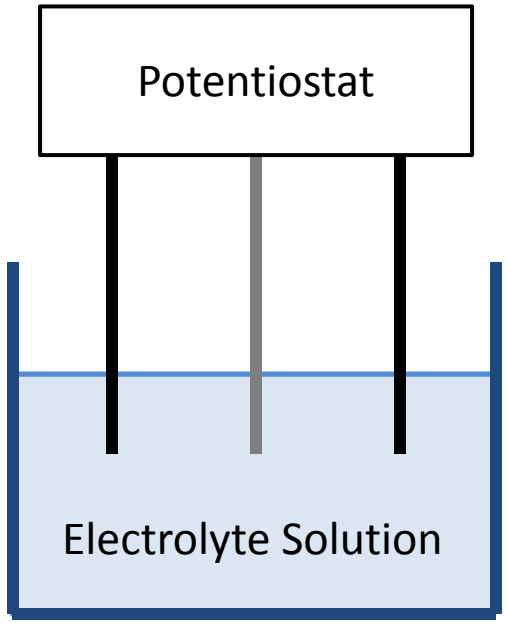
AQDS redox is reversible





[1] K. B. Oldham, J. C. Myland, *Electrochim. Acta*. **56**, 10612–10625 (2011).
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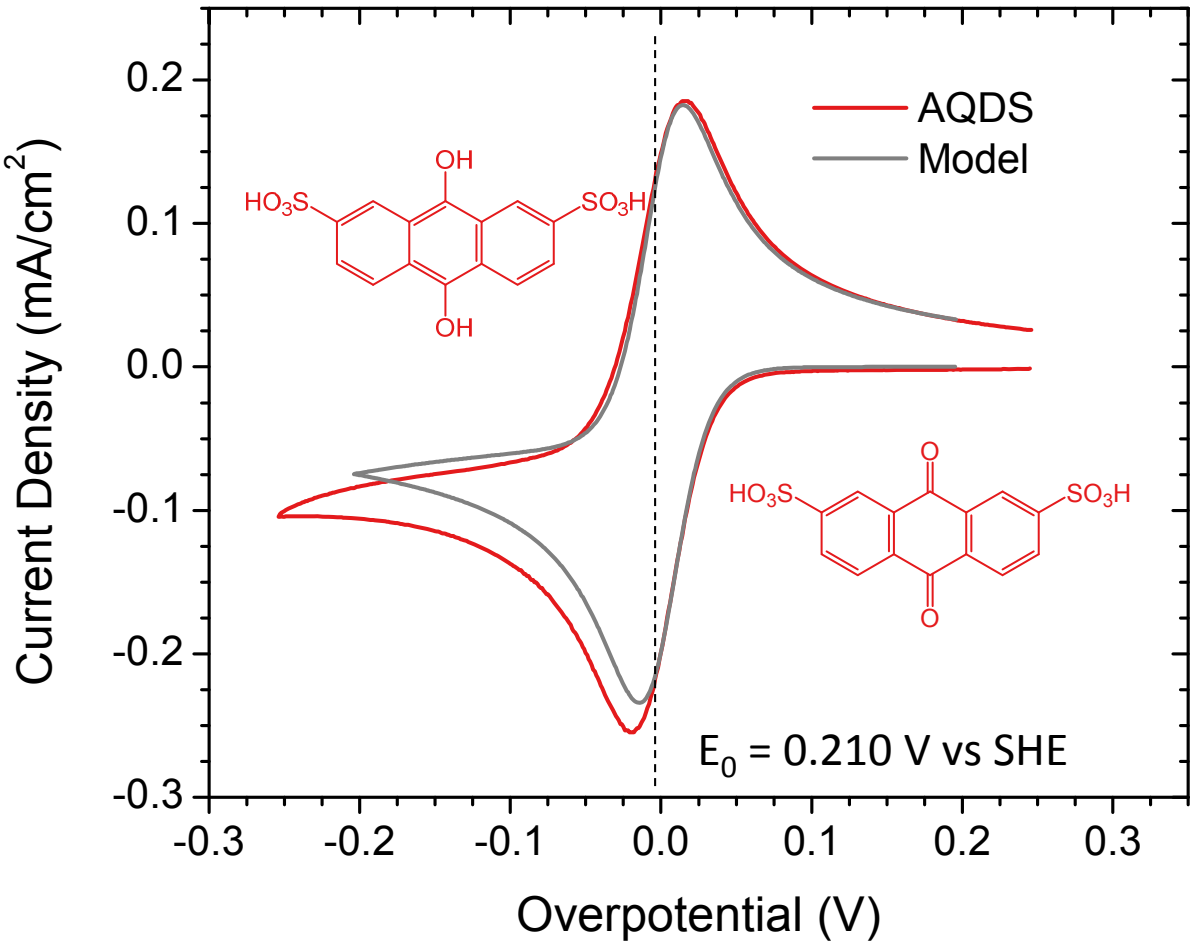

Reversible 2-electron model: assume AQDS concentration at electrode surface is dictated by Nernst equation [1]. Reaction rate is mass transport limited.

Measured rate constant $k_0 = 7.2 \times 10^{-3}$ cm/s [2]

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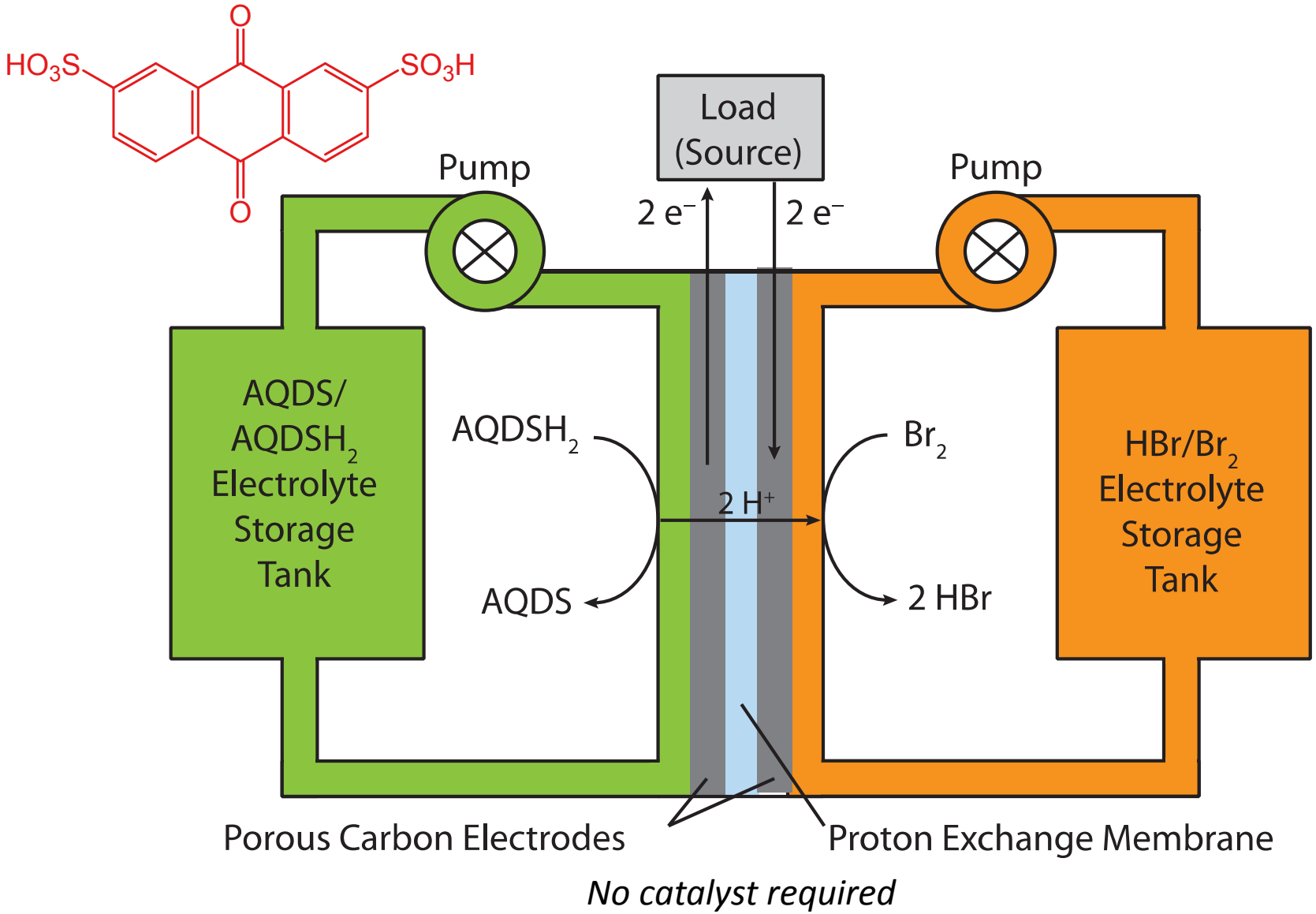
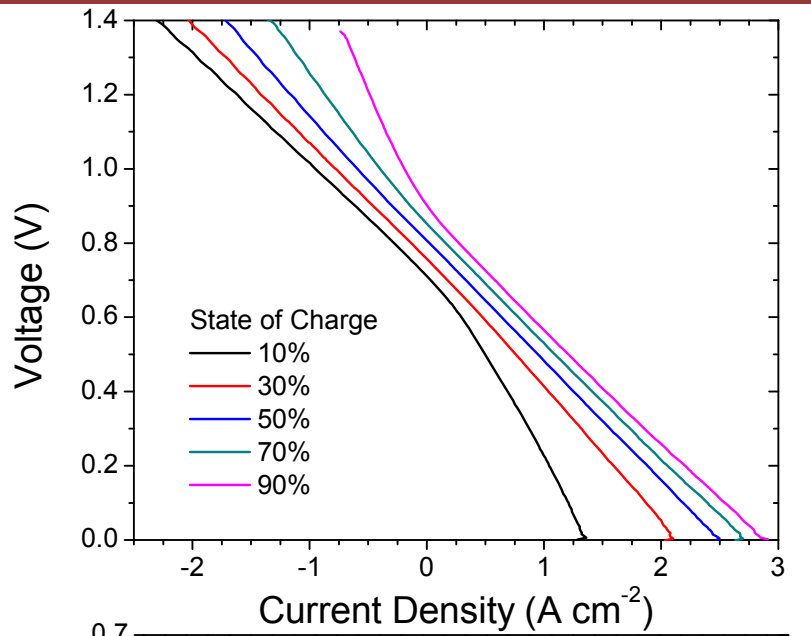
The Quinone – Bromine Flow Battery

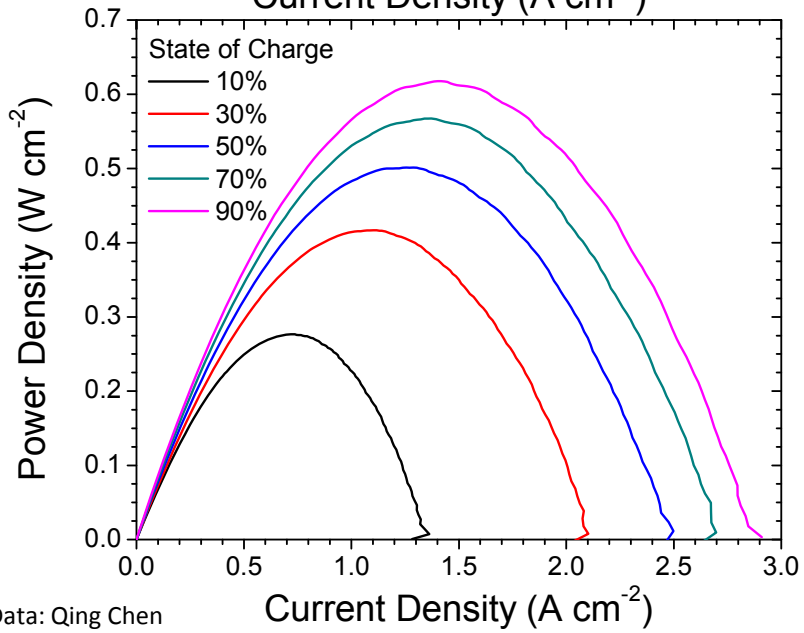


No catalyst required

Huskinson, B., Marshak, M. P., et al. (2014). *Nature*, *505*(7482), 195–198.

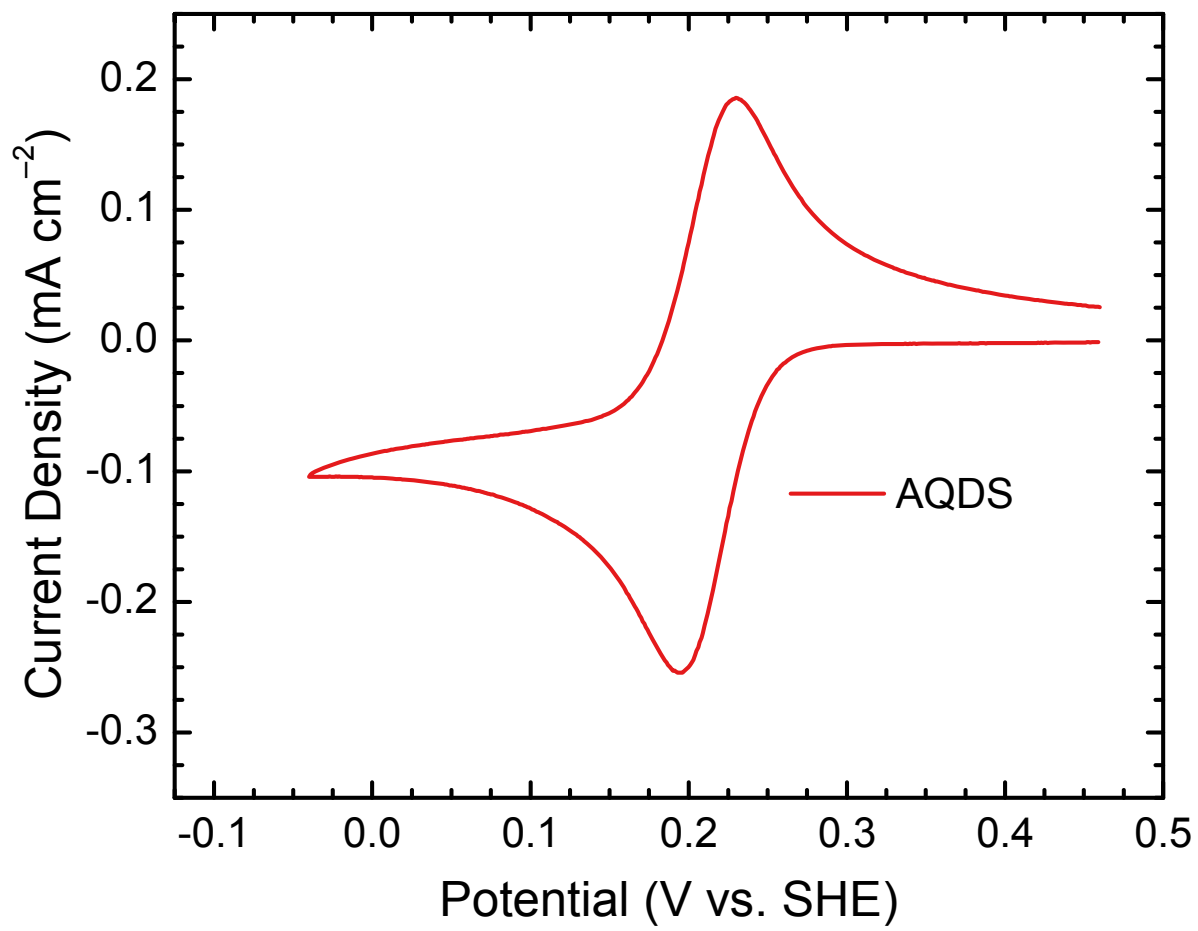
High Power Operation with AQDS/HBr battery

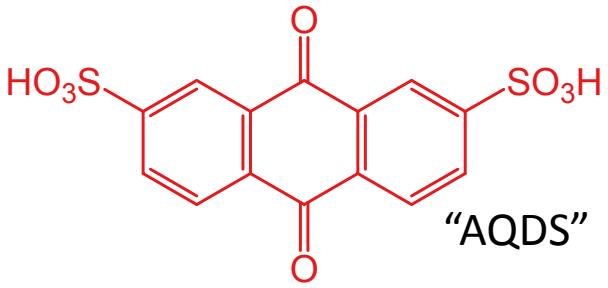




Data: Qing Chen

Increase Cell Voltage by Tuning Quinone Redox

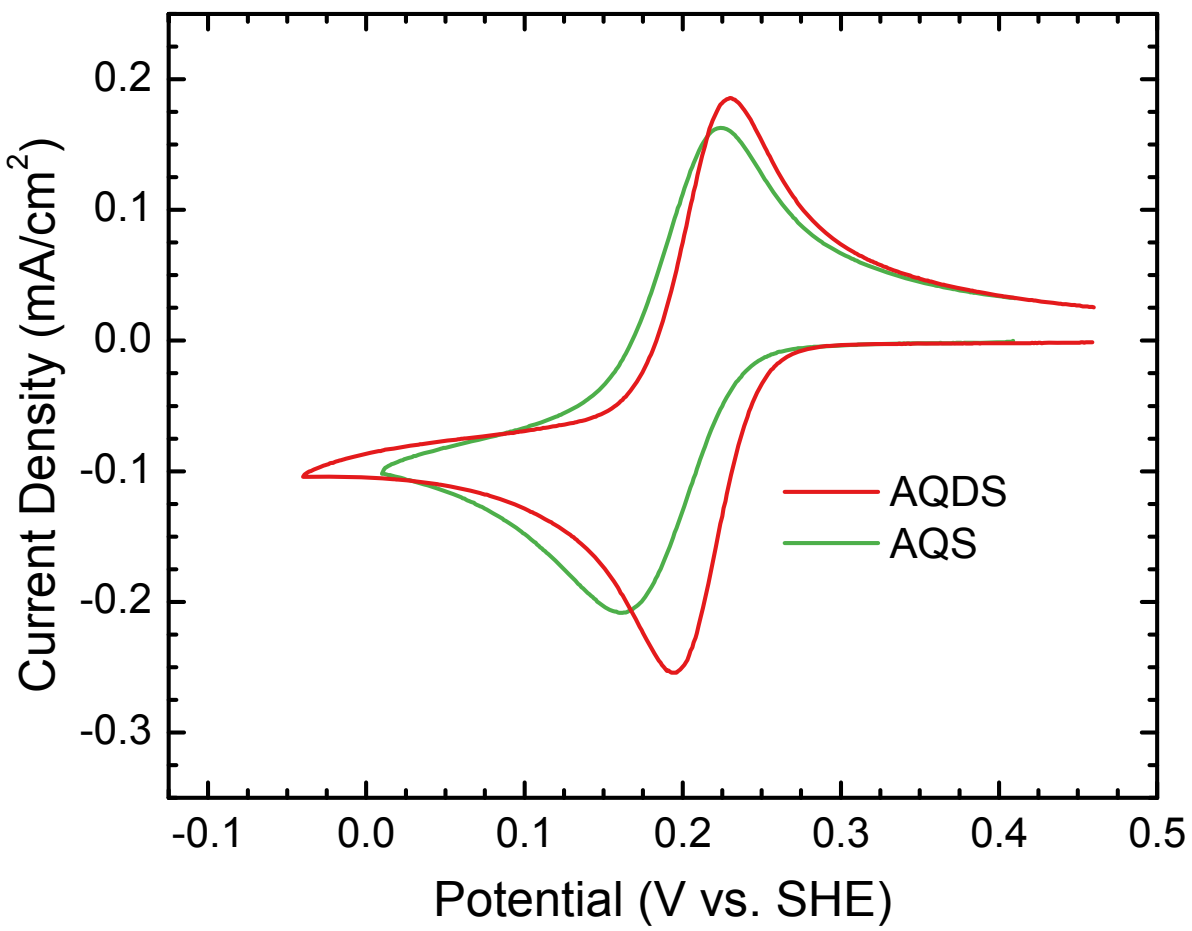


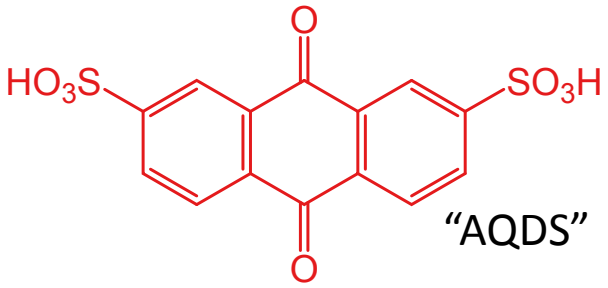


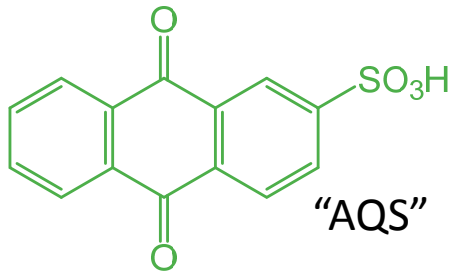
9,10-anthraquinone 2,7-disulfonic acid

Glassy carbon electrode, 3 mm dia, 25 mV/s scan rate, 25 °C. Ag/AgCl reference.
Pt coil counter electrode. Supporting electrolyte 1 M H_2SO_4
Quinone concentration 1 mM

Increase Cell Voltage by Tuning Quinone Redox



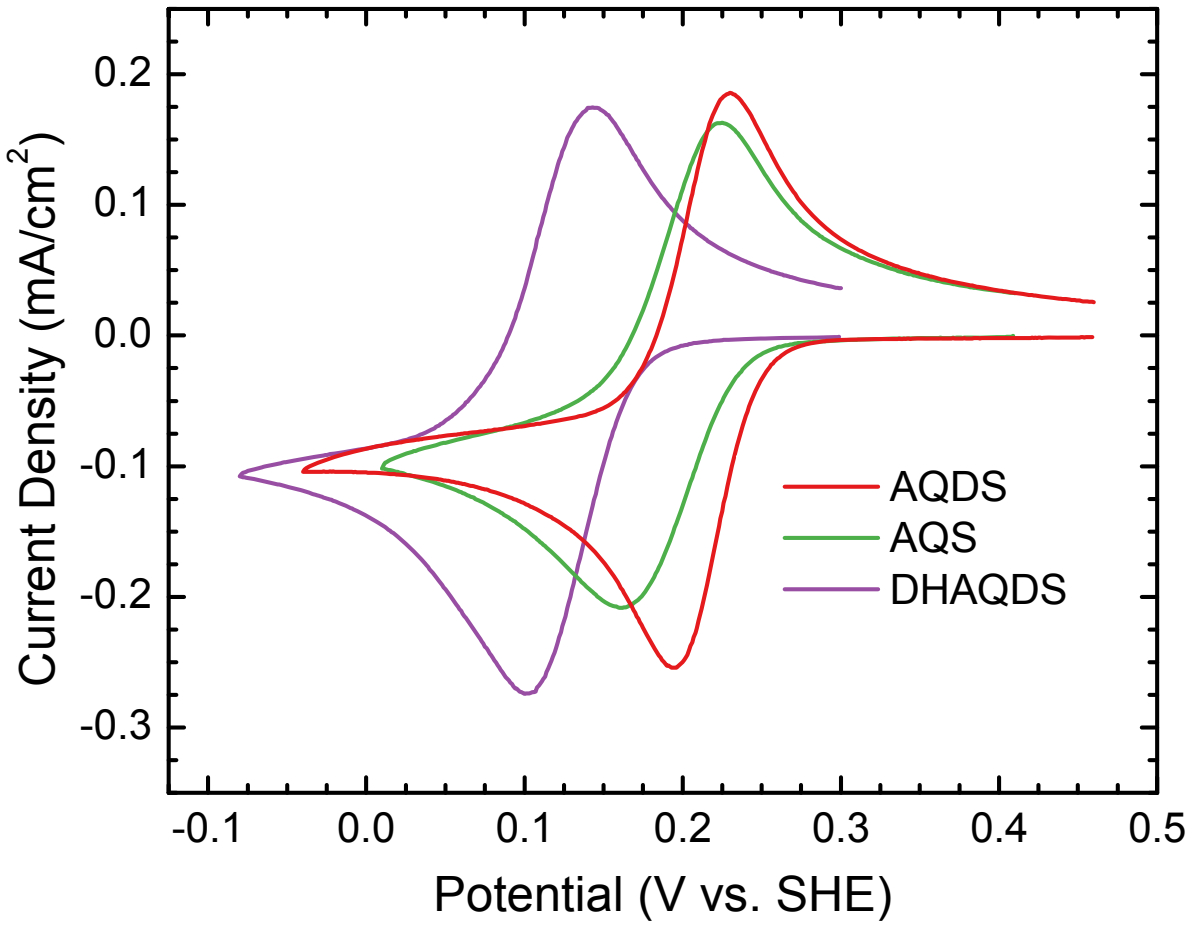


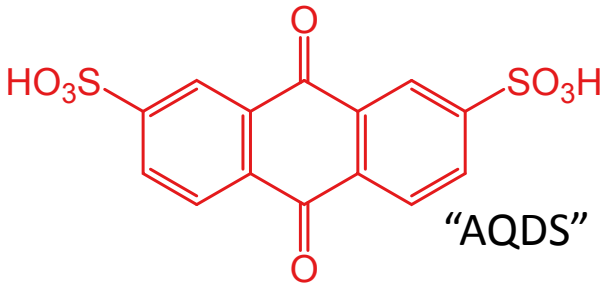


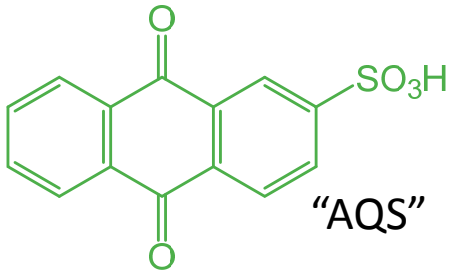
9,10-anthraquinone 2-sulfonic acid

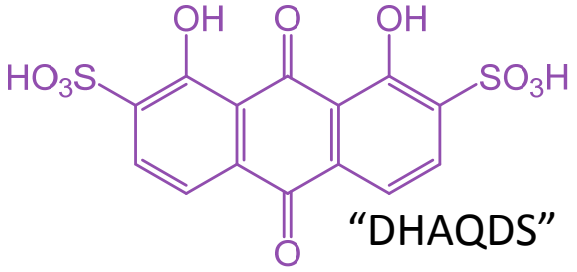
Glassy carbon electrode, 3 mm dia, 25 mV/s scan rate, 25 °C. Ag/AgCl reference.
Pt coil counter electrode. Supporting electrolyte 1 M H_2SO_4
Quinone concentration 1 mM

Increase Cell Voltage by Tuning Quinone Redox





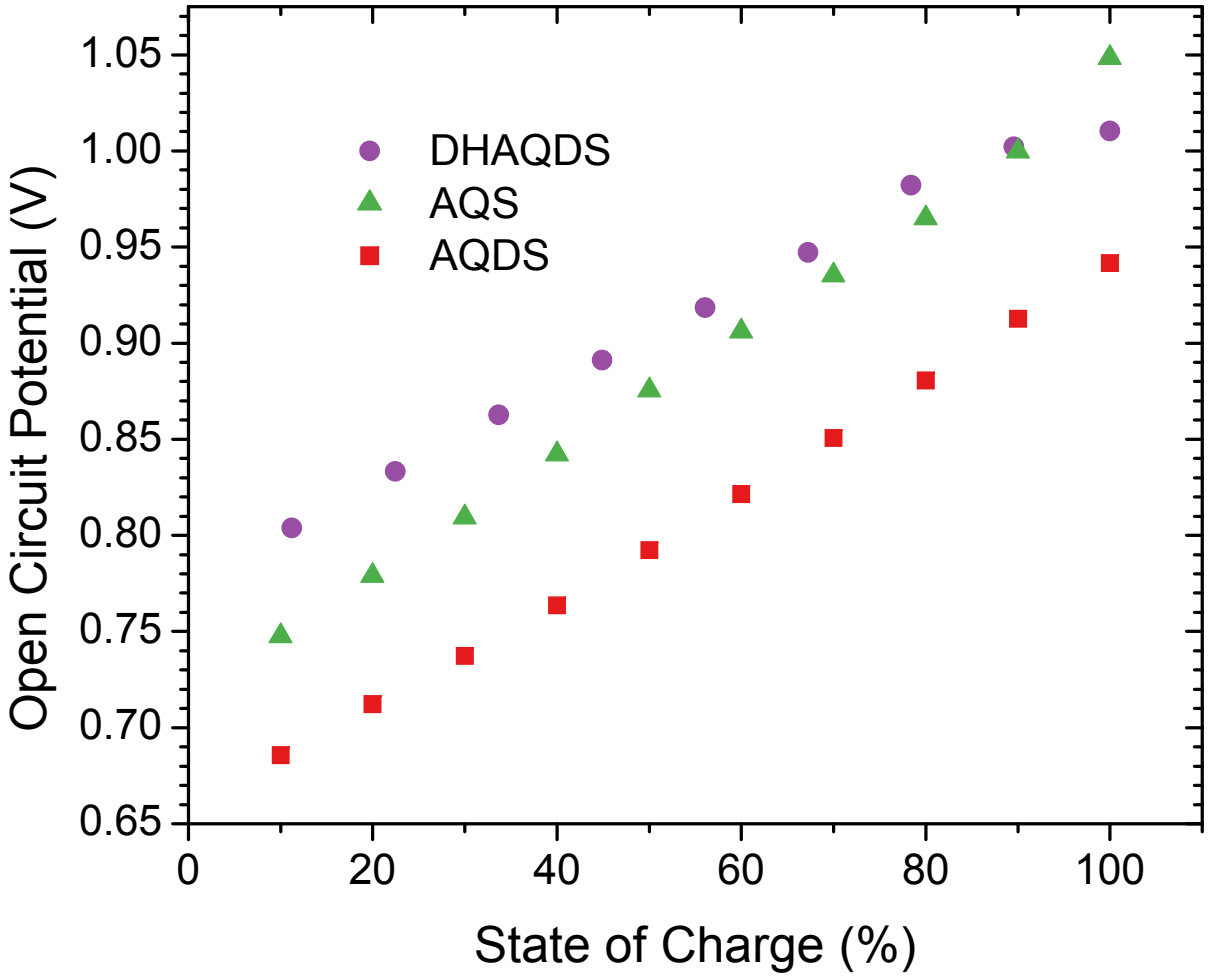


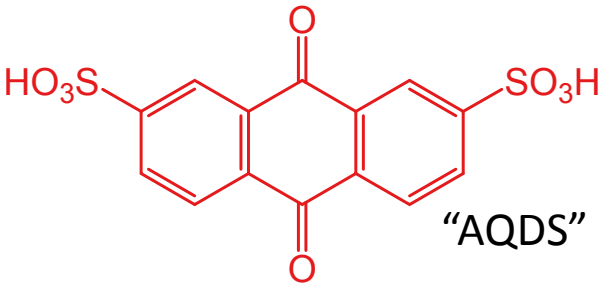


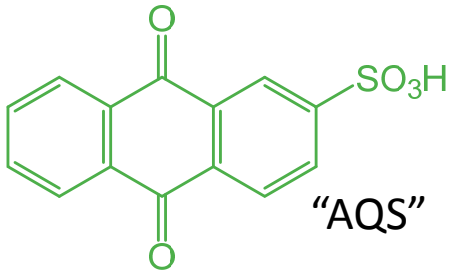
Glassy carbon electrode, 3 mm dia, 25 mV/s scan rate, 25 °C. Ag/AgCl reference. Pt coil counter electrode. Supporting electrolyte 1 M H_2SO_4
Quinone concentration 1 mM

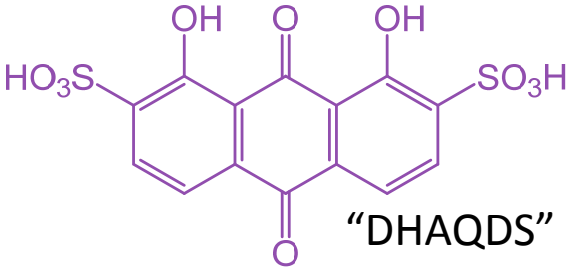
1,8-dihydroxy 9,10-anthraquinone 2,7-disulfonic acid

Increase Cell Voltage by Modifying Molecules



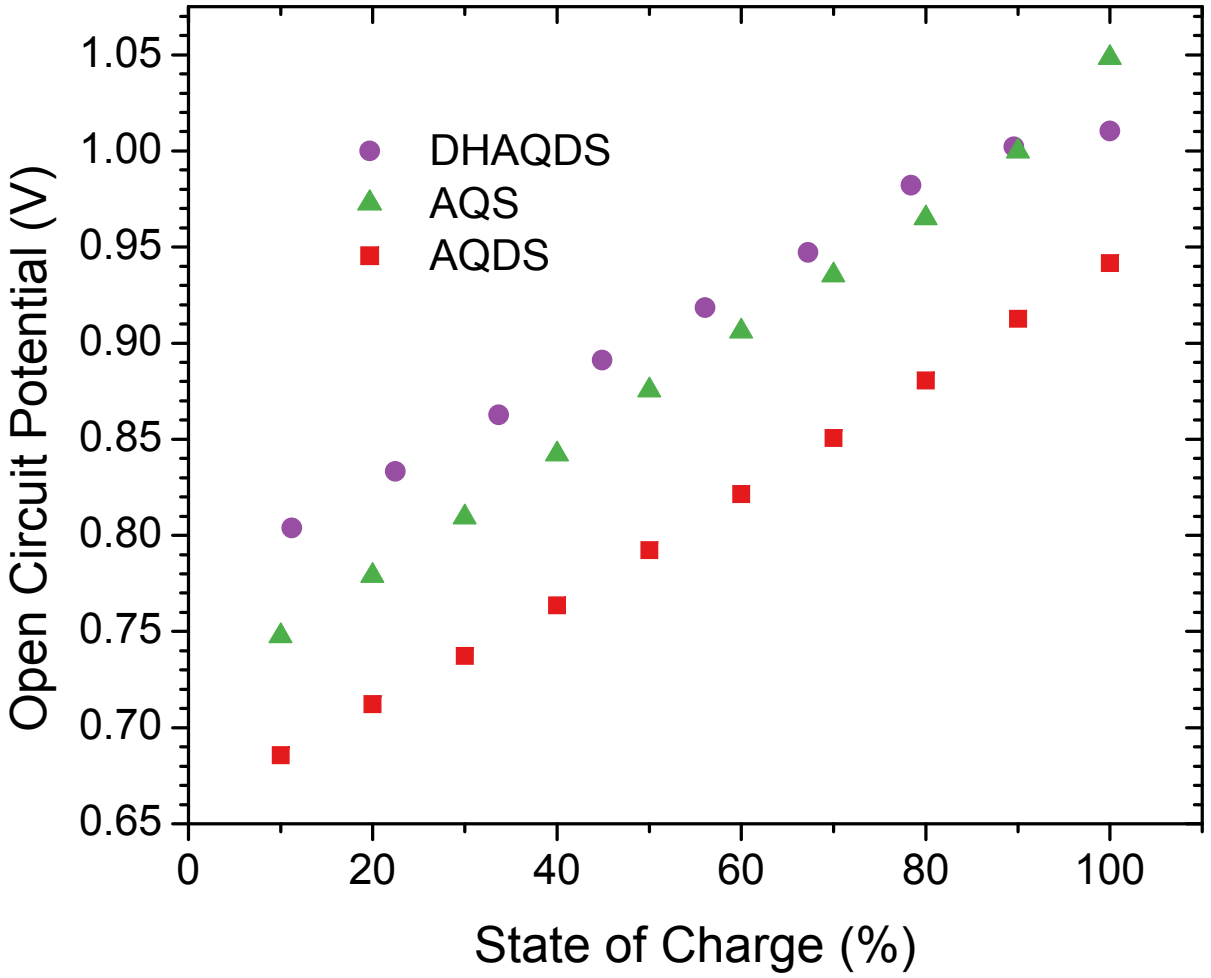


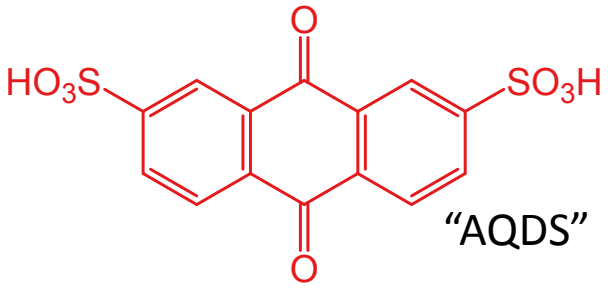


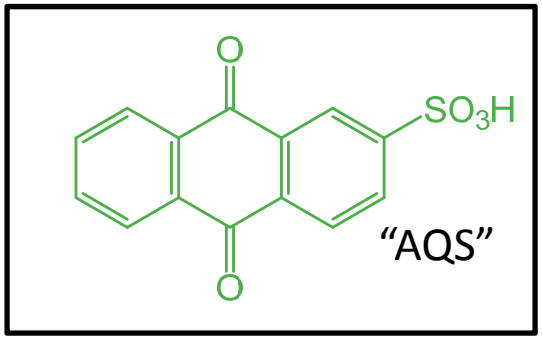


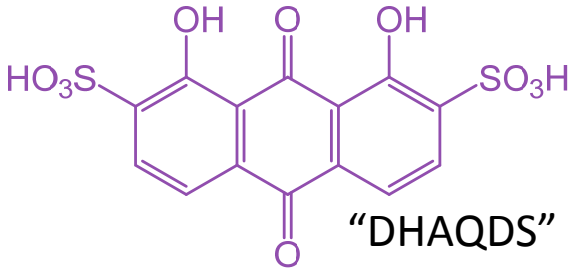
Posolyte: 0.5 M Br_2, 3 M HBr
Negolyte: 1 M quinone, 1 to 2 M H_2SO_4 (3 M total proton concentration)

Increase Cell Voltage by Modifying Molecules









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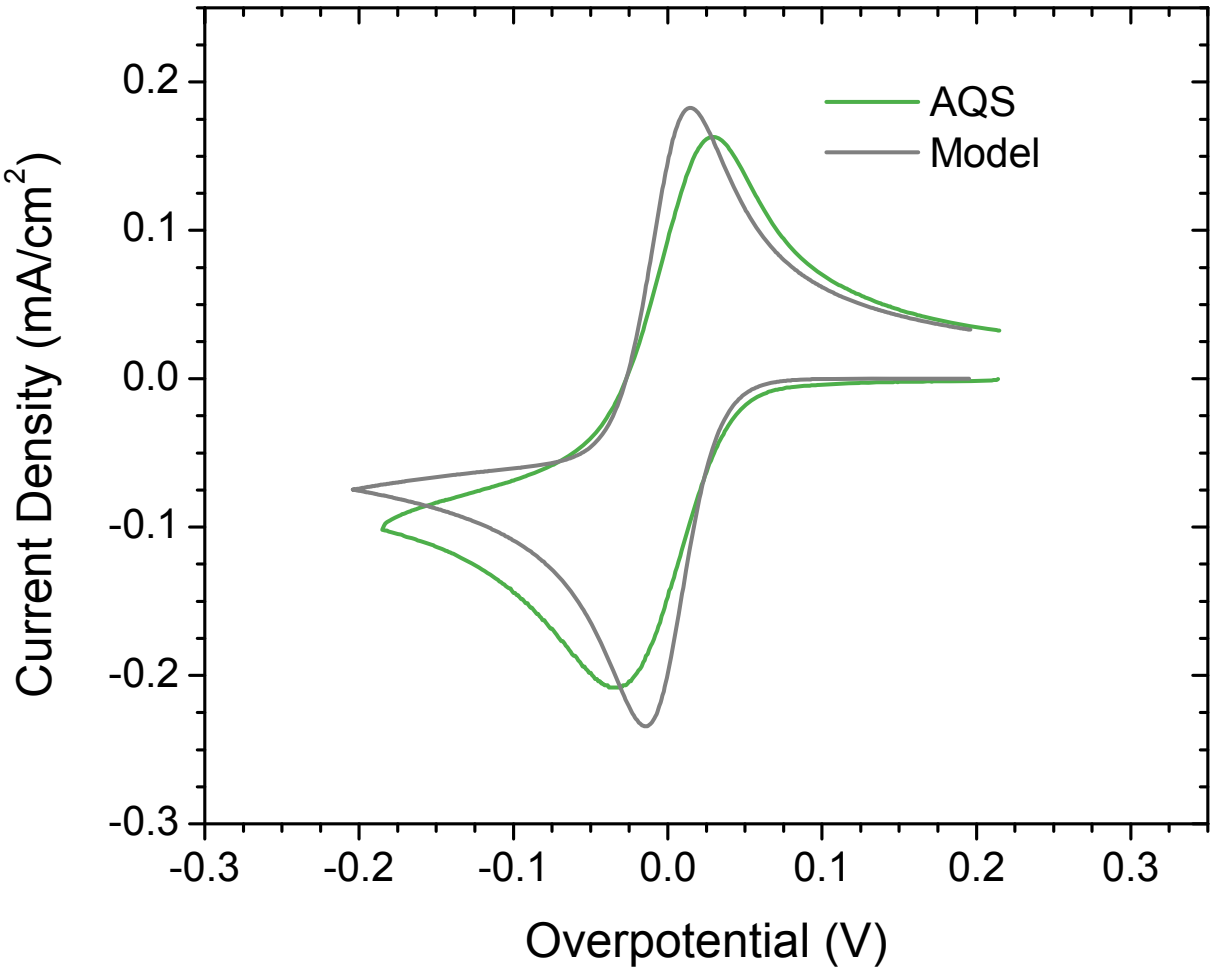
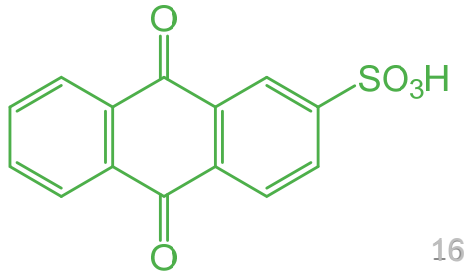
AQS redox is not quite reversible



Reversible 2-electron model: assume AQS concentration at electrode surface is dictated by Nernst equation [1]. Reaction rate is mass transport limited.



Glassy carbon electrode, 3 mm dia, 25 mV/s scan rate, 25 °C. Ag/AgCl reference. Pt coil counter electrode. Supporting electrolyte 1 M H_2SO_4. Quinone concentration 1 mM

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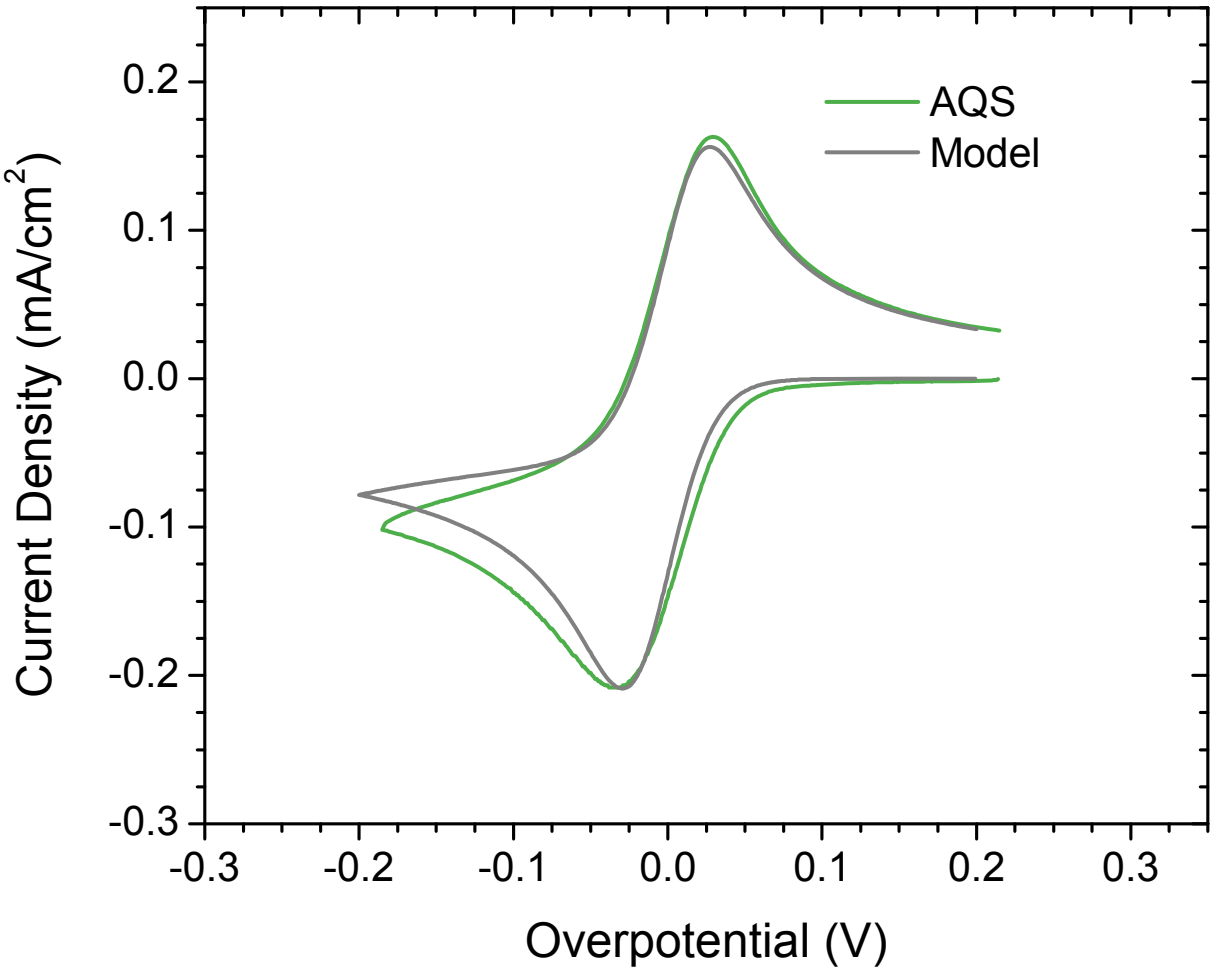
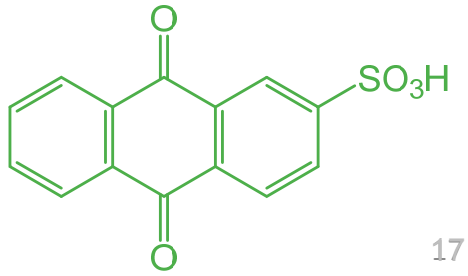


Quasireversible model: Assume Butler-Volmer kinetics with a rate constant $k_0 = 2 \times 10^{-3}$ cm/s [1].



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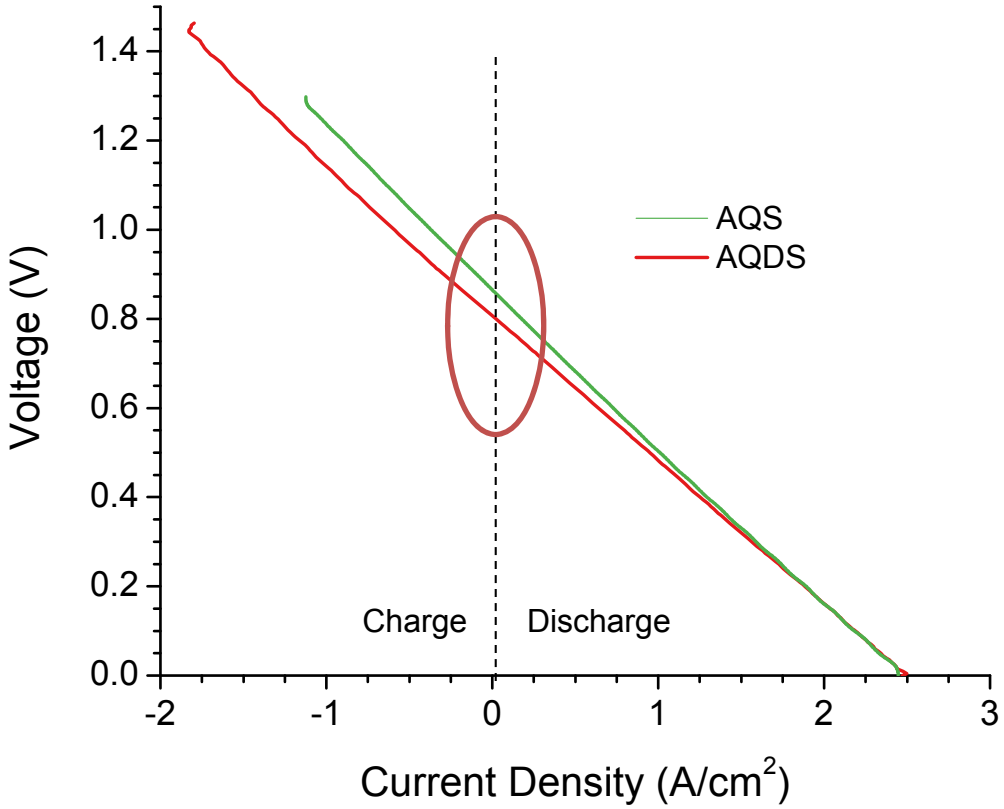
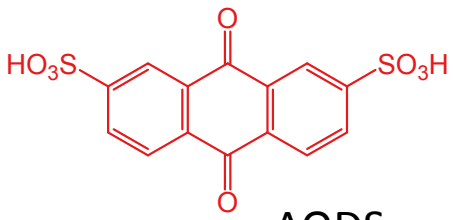
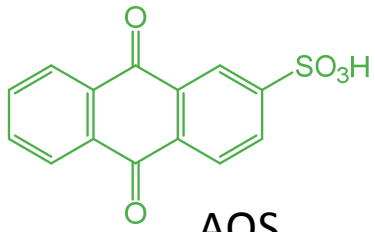
Switching Molecules Leads to Higher Power





AQDS



AQS

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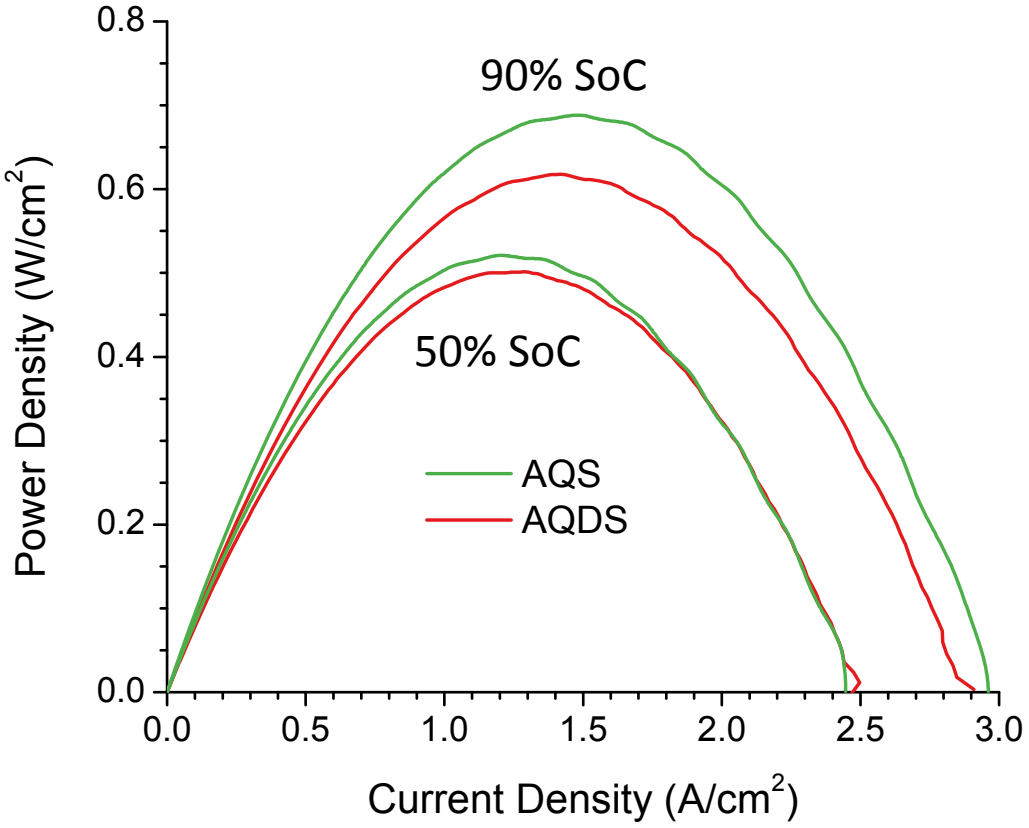

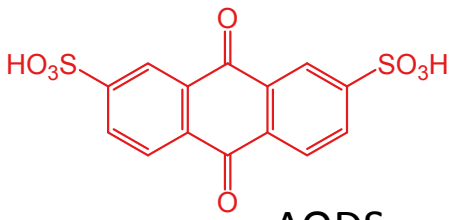

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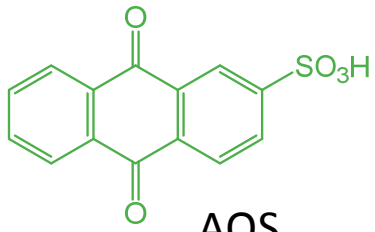

AQS

Posolyte: 0.5 M Br_2, 3 M HBr

pH affects AQDS electrochemistry

$$AQ + (N_{H^+})H^+ + (N_{e^-})e^- \rightarrow H_{(N_{H^+})}AQ^{\pm z}$$

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$$E = E^{0'} + \frac{RT}{(N_{e^-})F}\ln\left(\frac{[AQ][H^+]^{N_{H^+}}}{[H_mAQ^{\pm z}]}\right)$$

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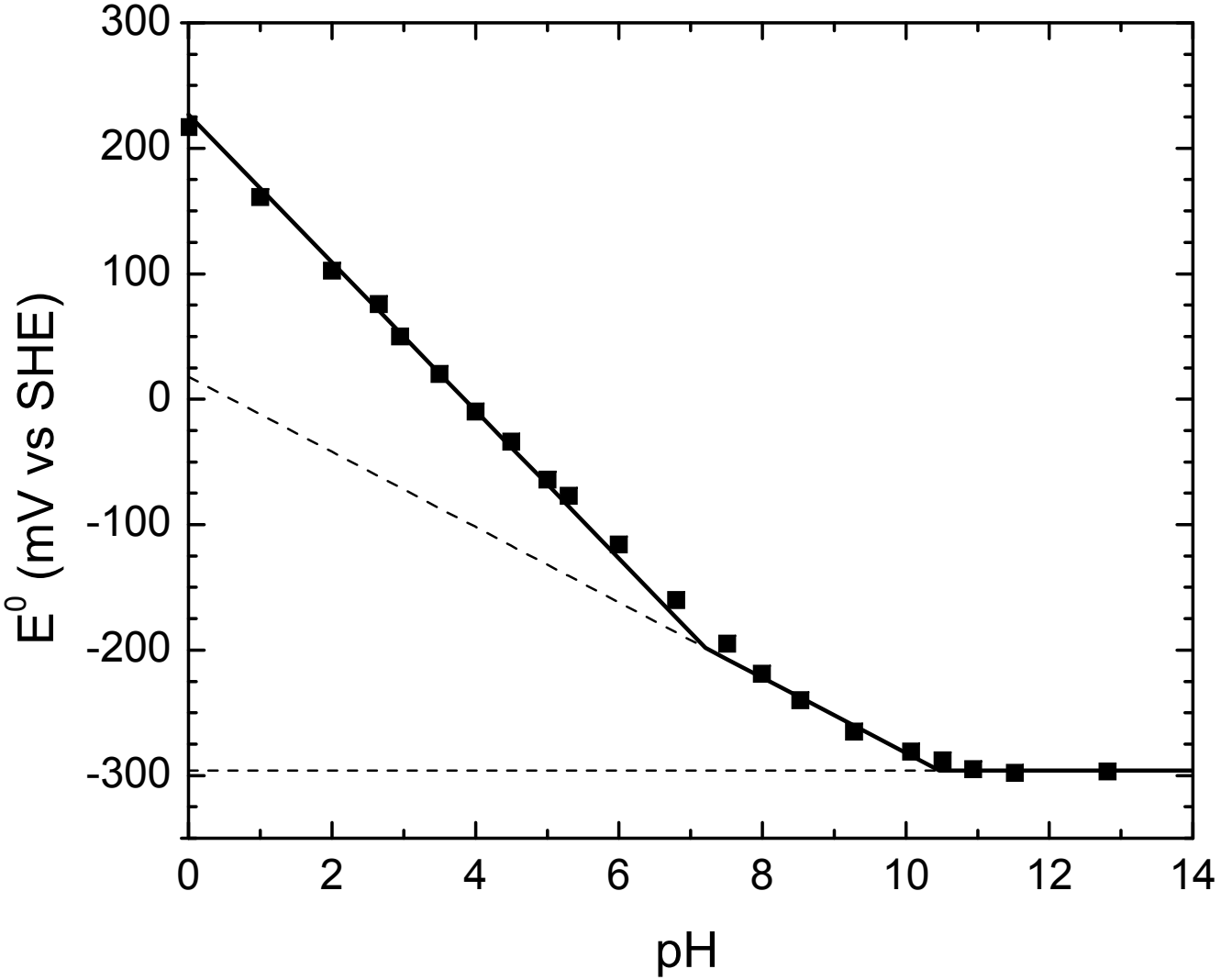
$$E = E^{0'} - \frac{RT}{F}\left(\frac{N_{H^+}}{N_{e^-}}\right)(\mathrm{p}H) + C$$

pH affects AQDS electrochemistry



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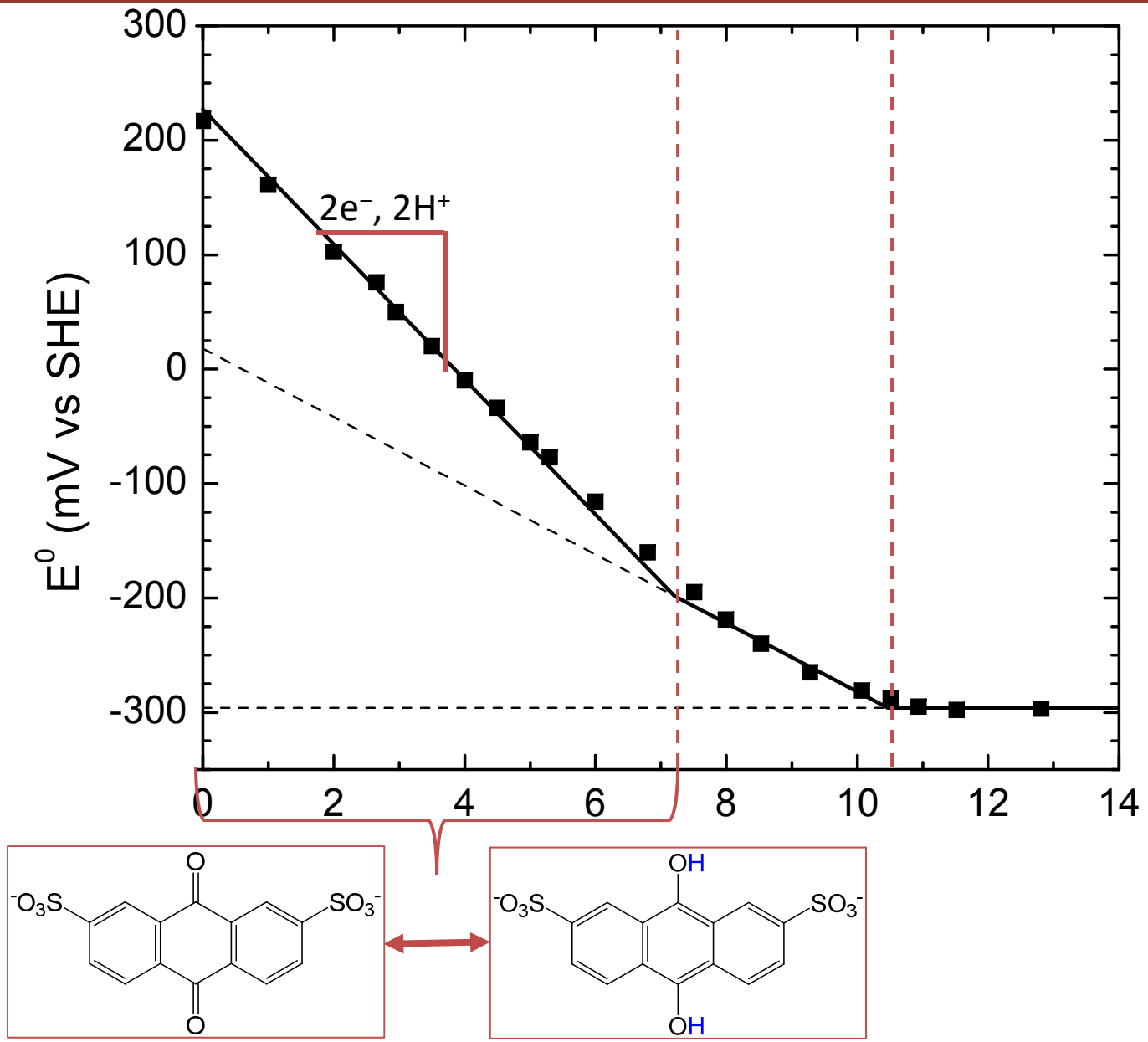
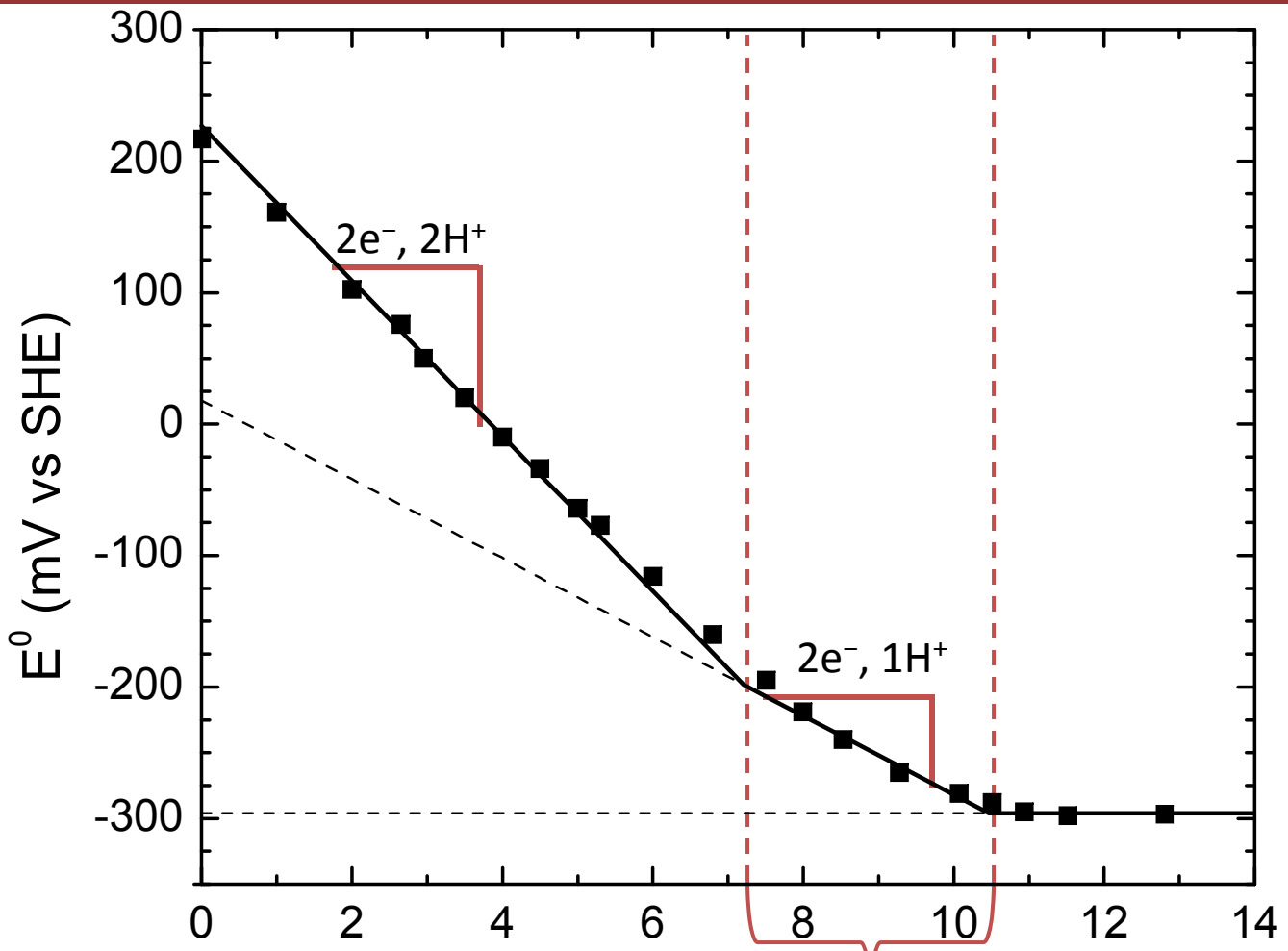
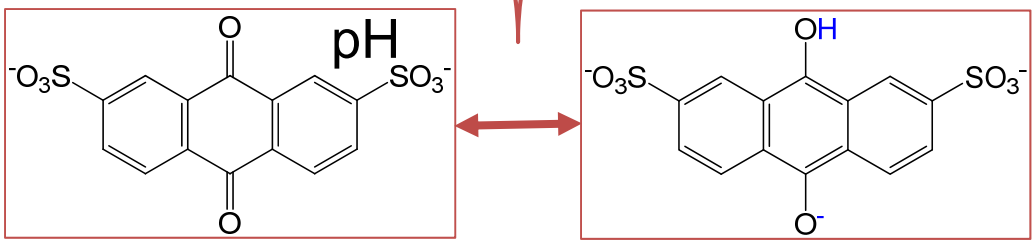


pKa_1 = 7.70,
pKa_2 = 10.52
E^0 = 0.229 V
$E^0_{dianion}$ = −0.313 V

pH affects AQDS electrochemistry





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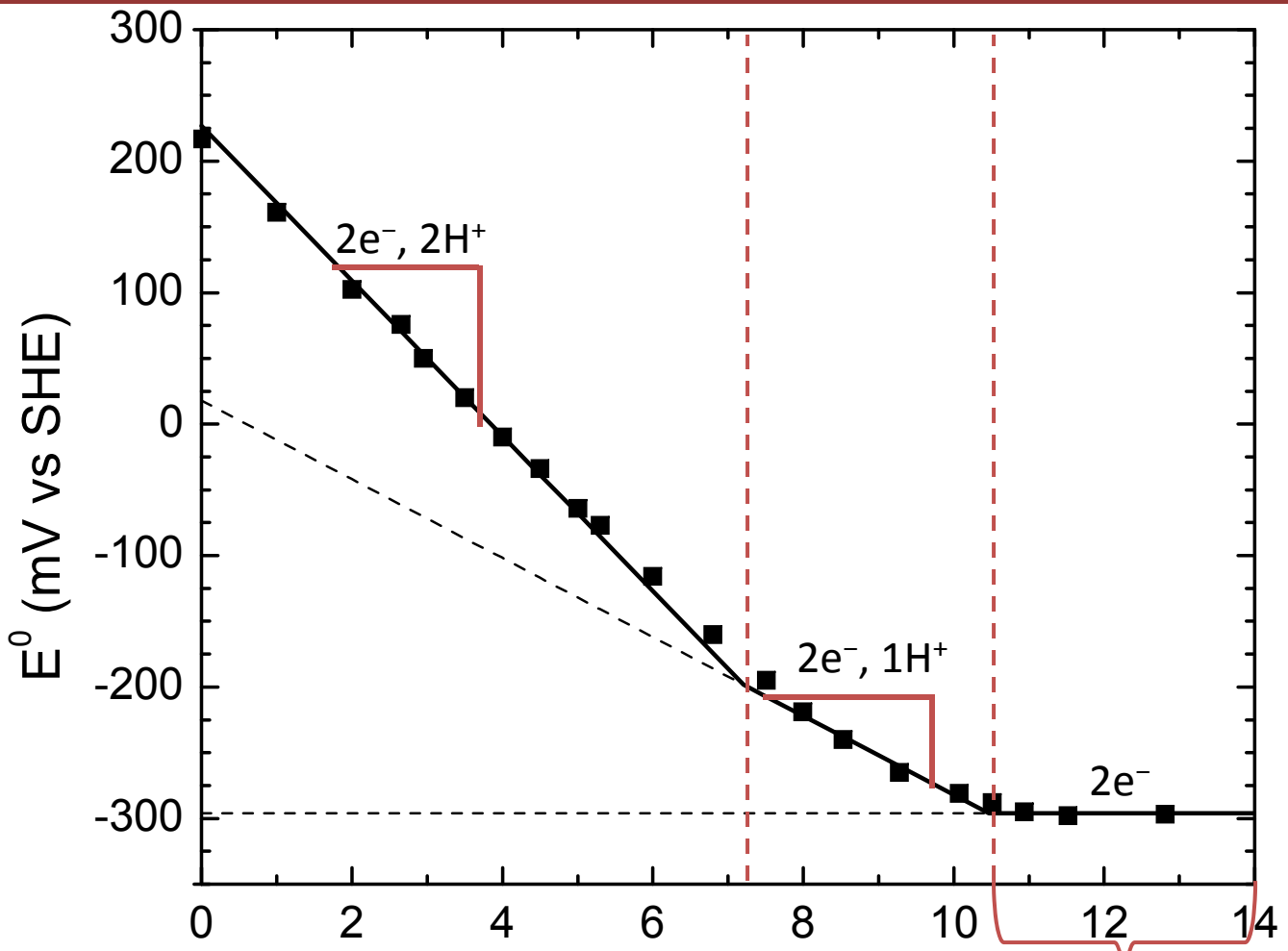
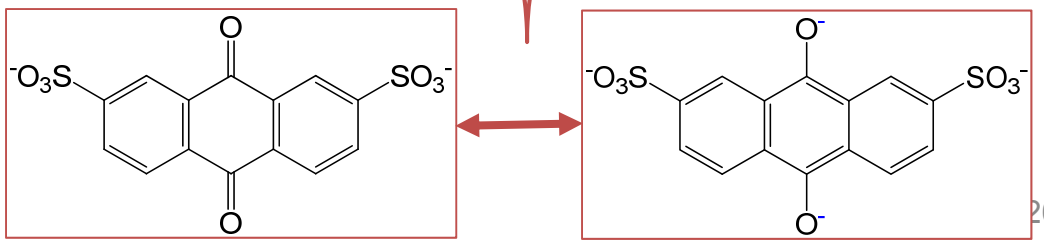
pKa_2 = 10.52
E^0 = 0.229 V
$E^0_{dianion}$ = −0.313 V

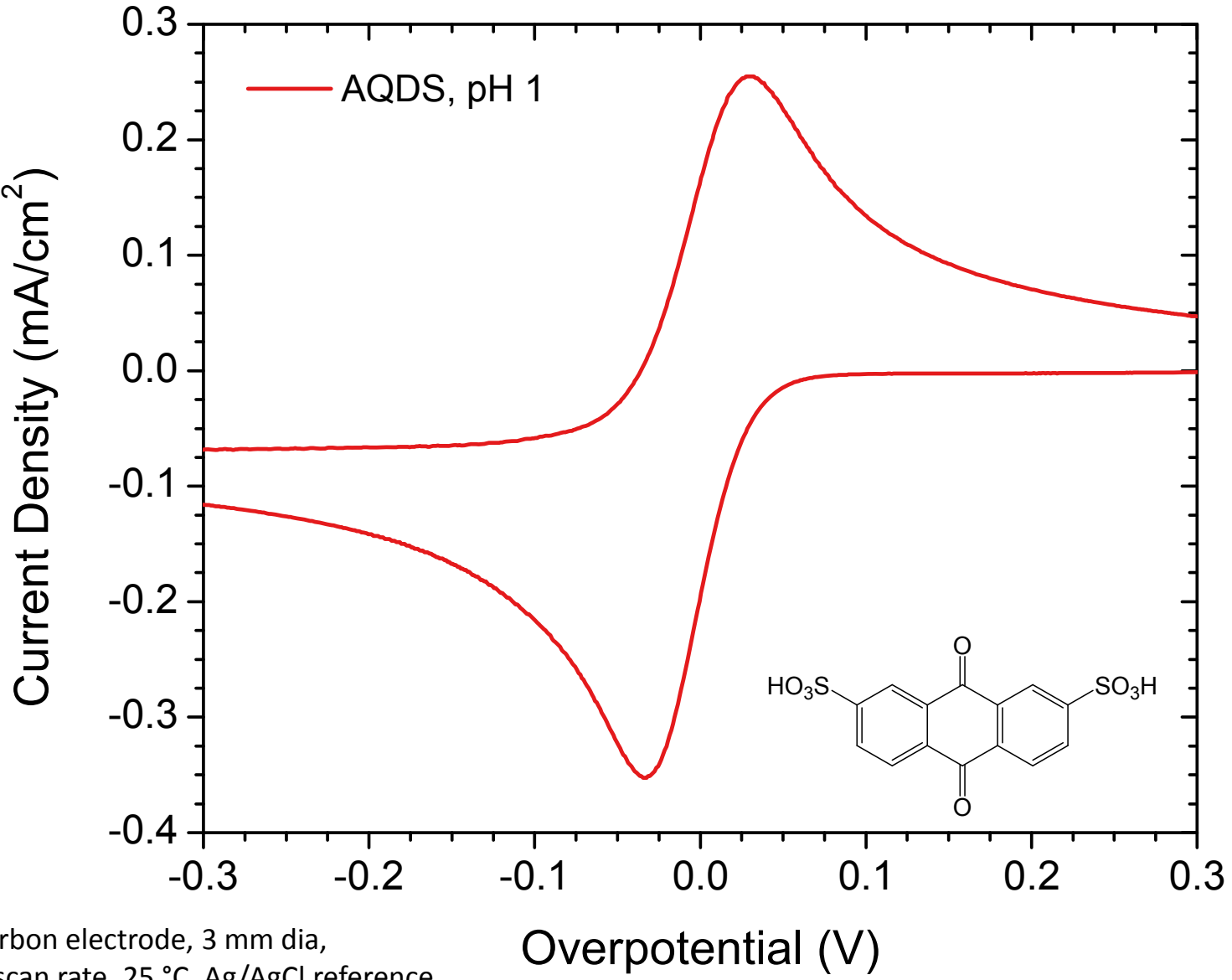
pH affects AQDS electrochemistry



pKa_1 = 7.70,
pKa_2 = 10.52
E^0 = 0.229 V
$E^0_{dianion}$ = −0.313 V

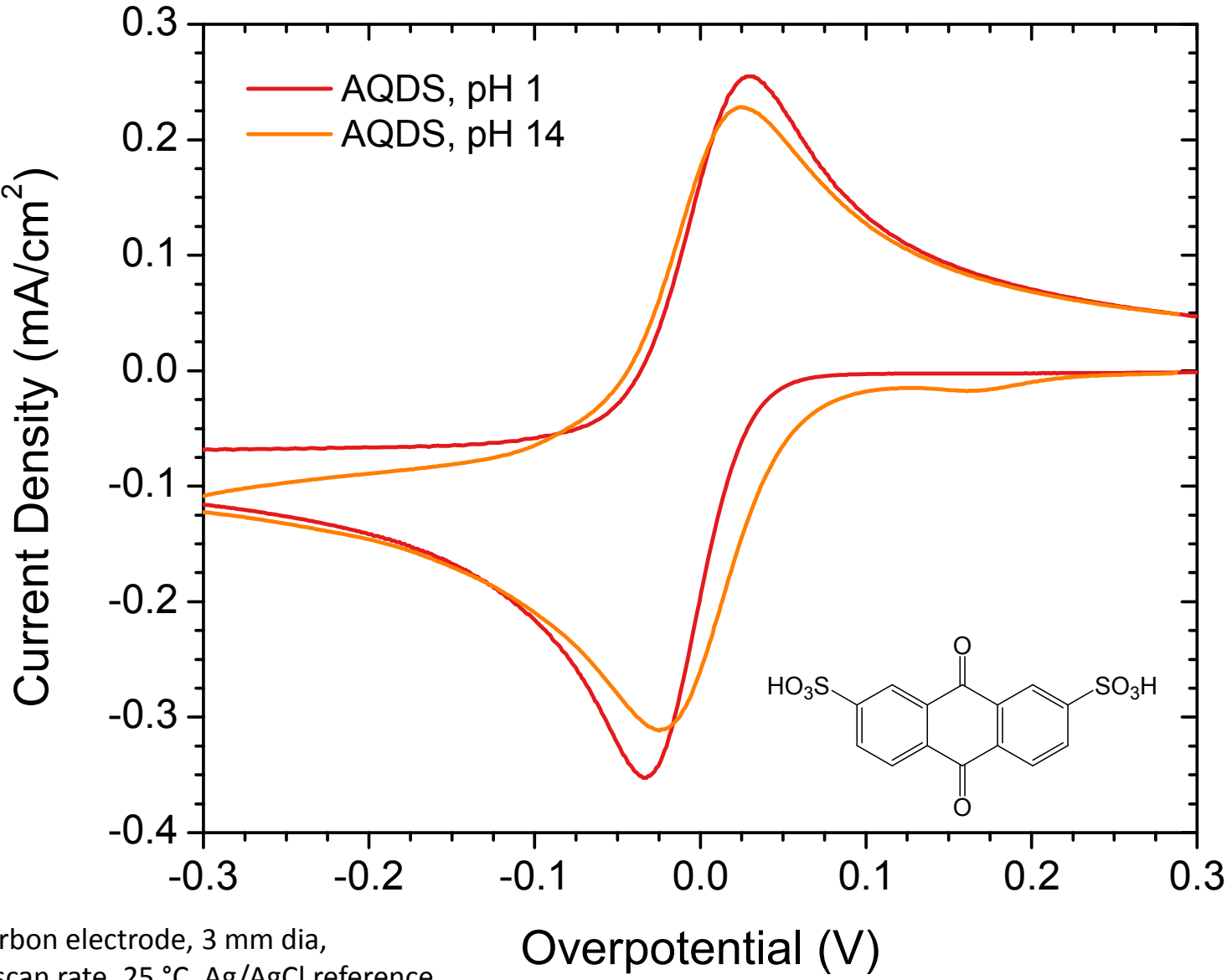


AQDS reduction kinetics as function of pH



Glassy carbon electrode, 3 mm dia,
50 mV/s scan rate, 25 °C. Ag/AgCl reference.
Pt coil counter electrode. Supporting electrolyte H_2SO_4 or KOH. Quinone concentration 1 mM

AQDS reduction kinetics as function of pH



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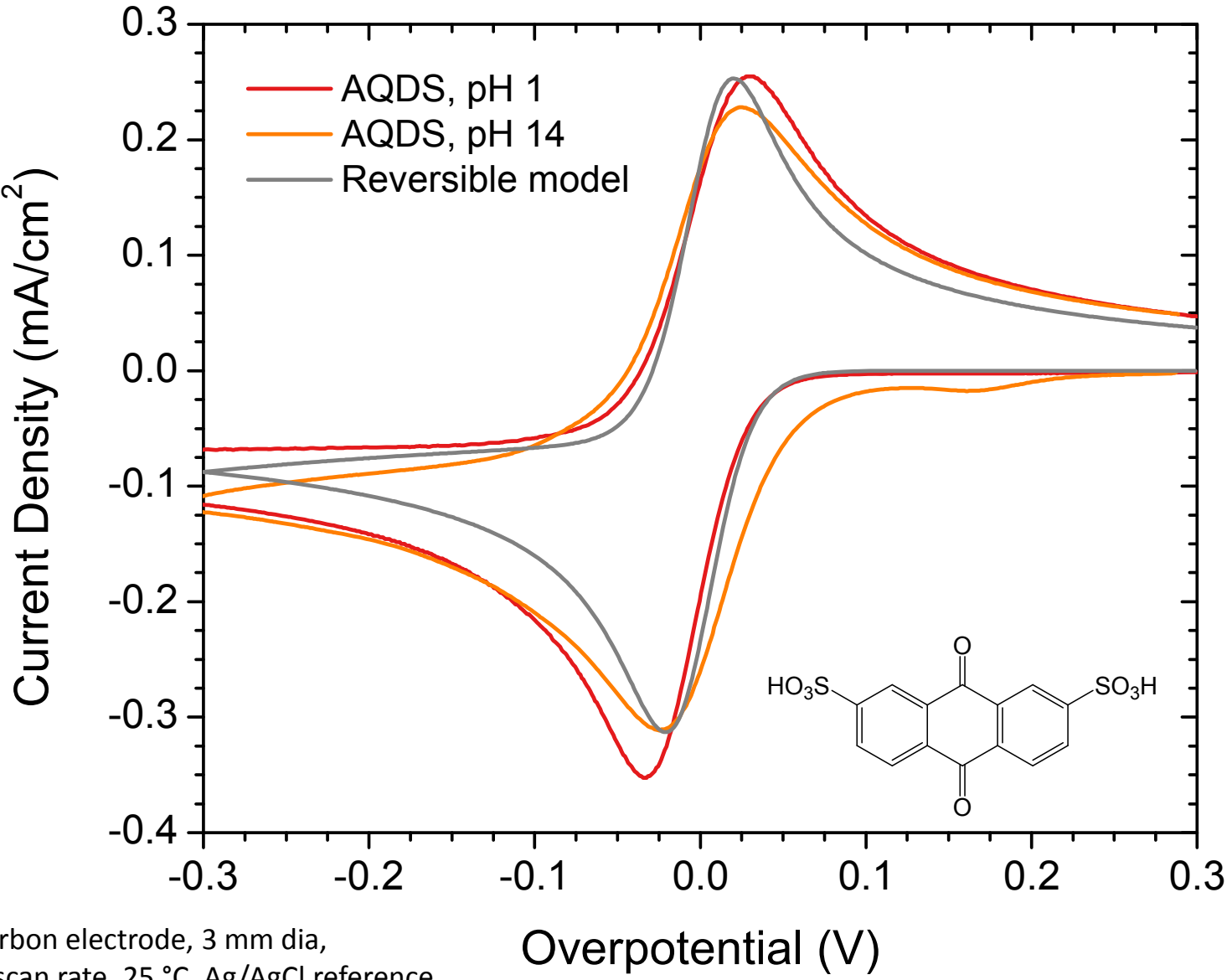
AQDS reduction kinetics as function of pH



Glassy carbon electrode, 3 mm dia,
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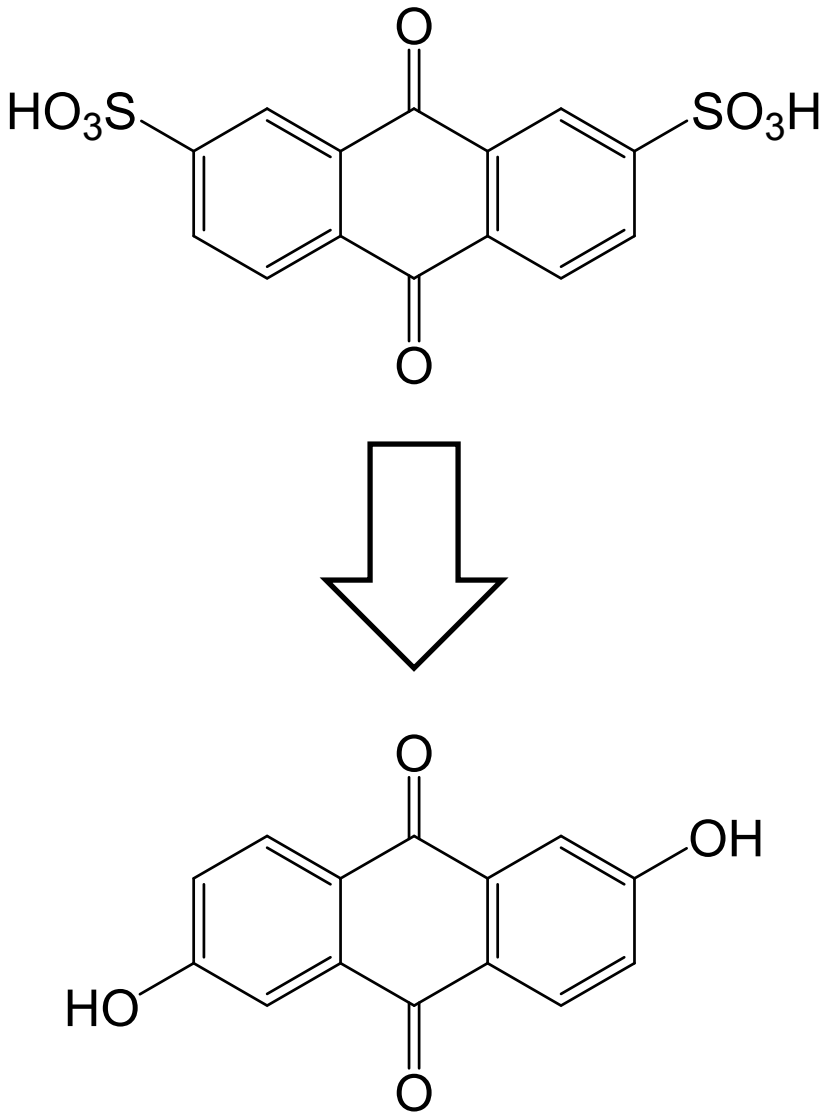
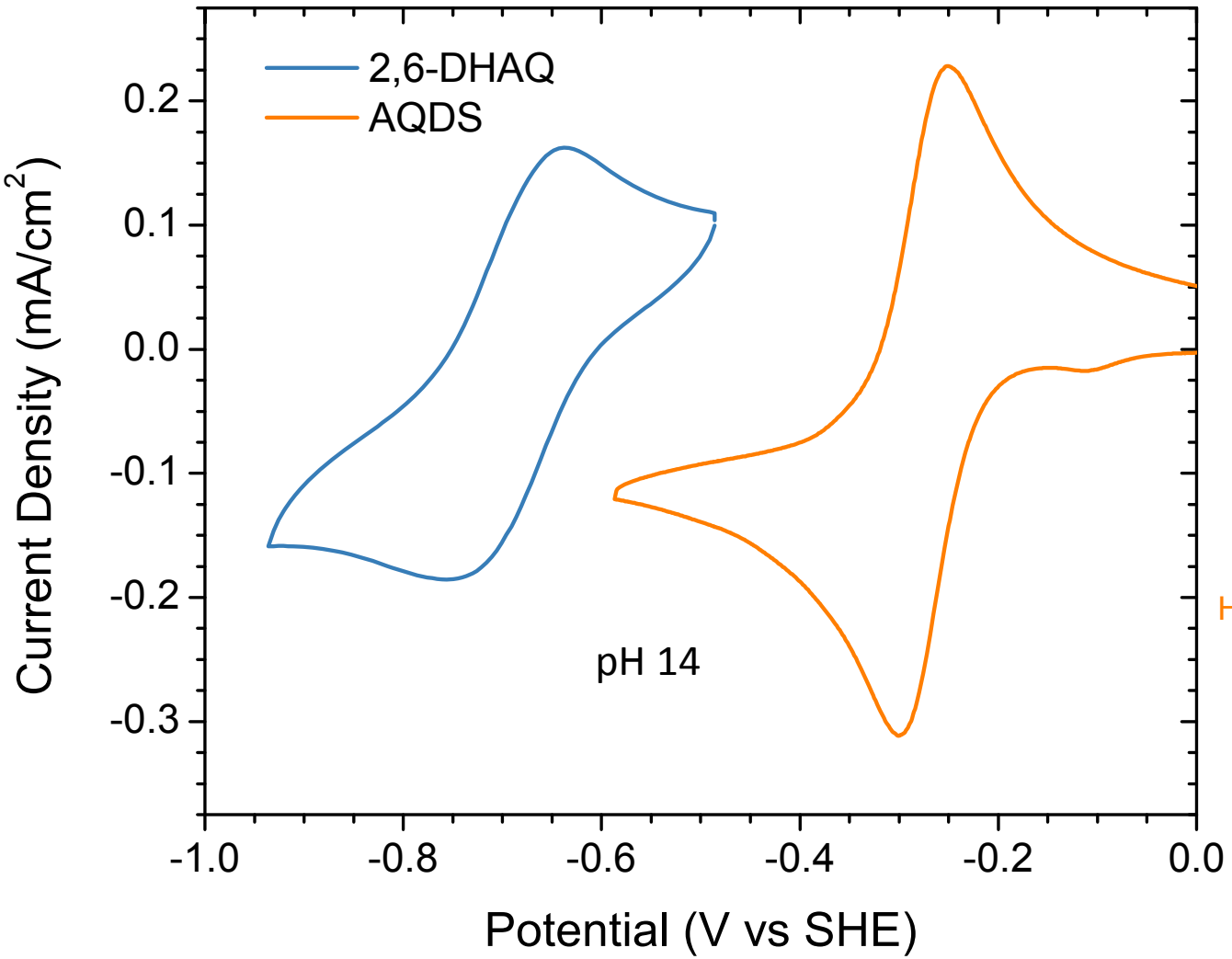
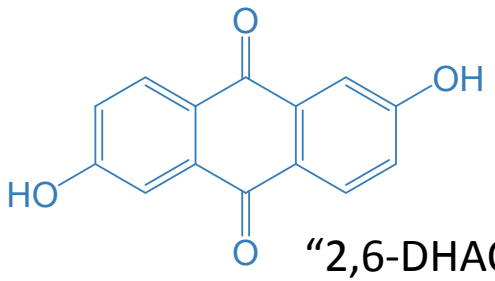
Pt coil counter electrode. Supporting electrolyte H_2SO_4 or KOH. Quinone concentration 1 mM

Optimizing molecule for basic solutions



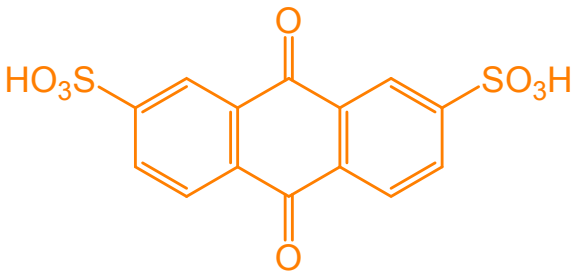
Optimizing molecule for basic solutions



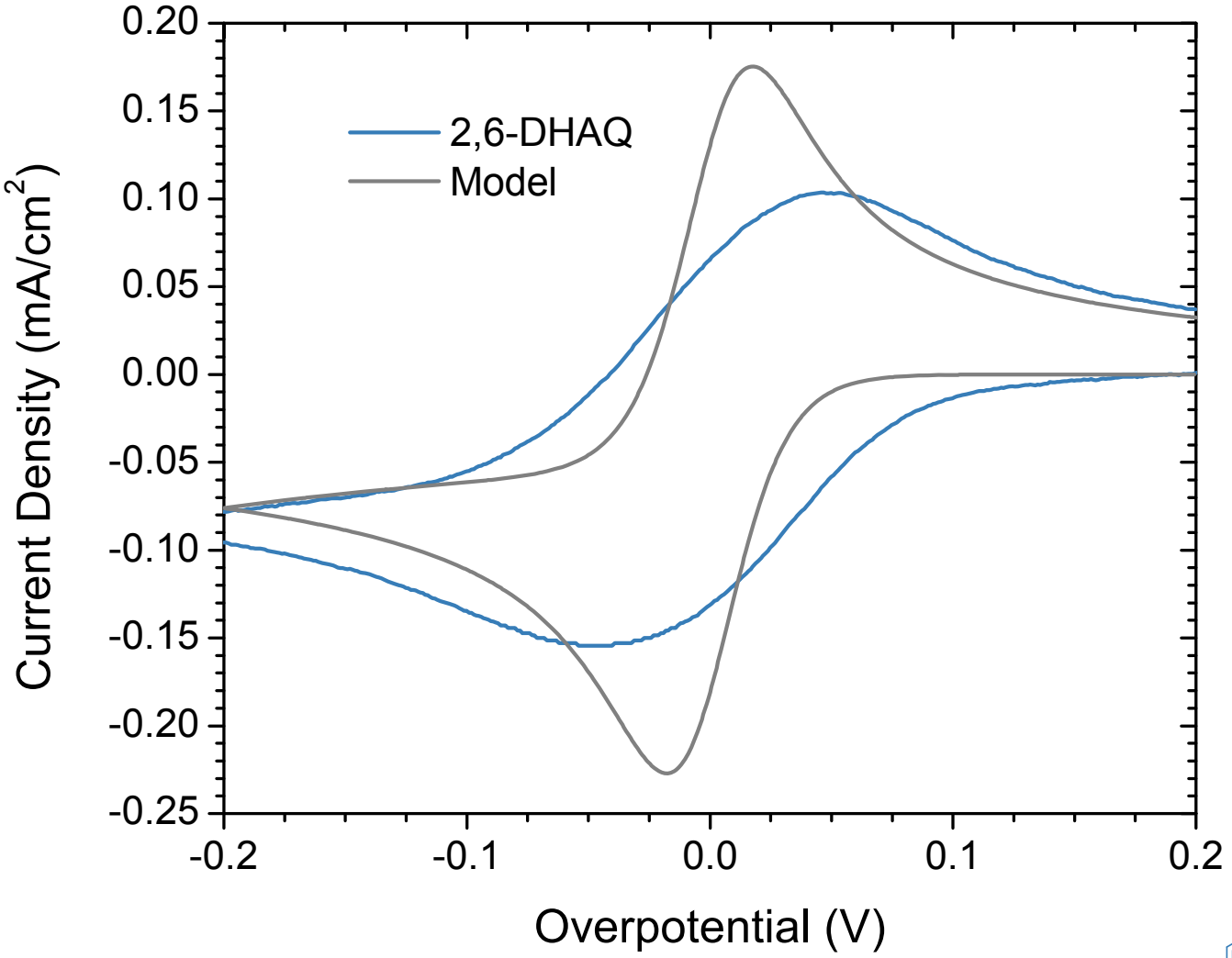


"2,6-DHAQ"

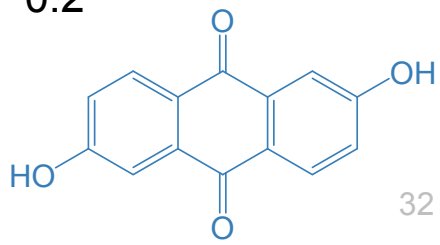
2,6-dihydroxy 9,10-anthraquinone



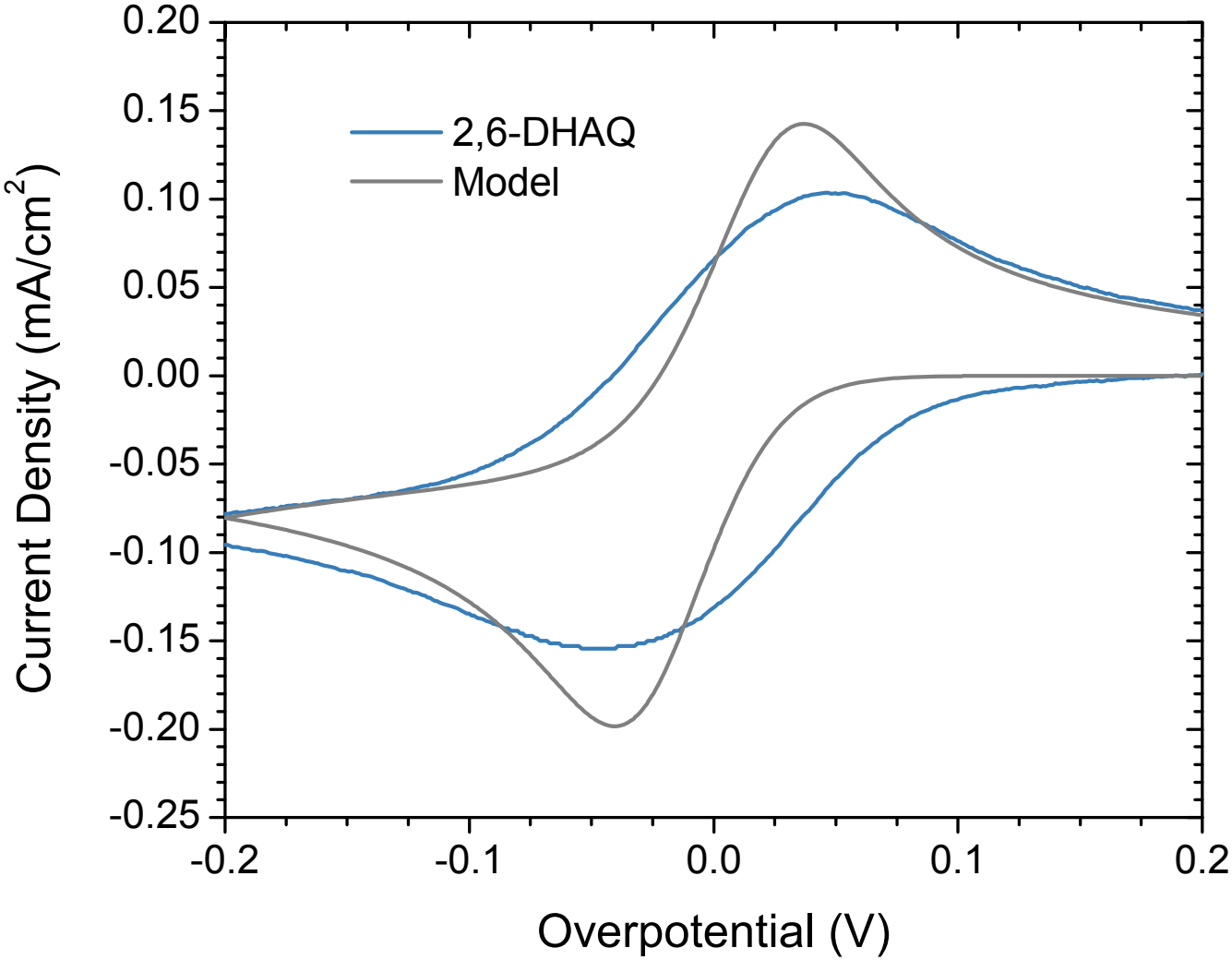
Two-electron transfer model can't explain CV



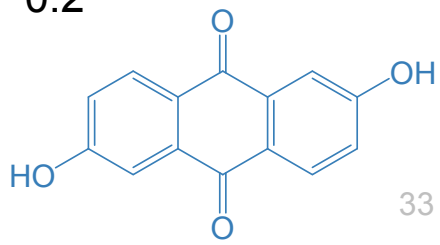
$k_0 = 1 \times 10^{-2}$ cm/s



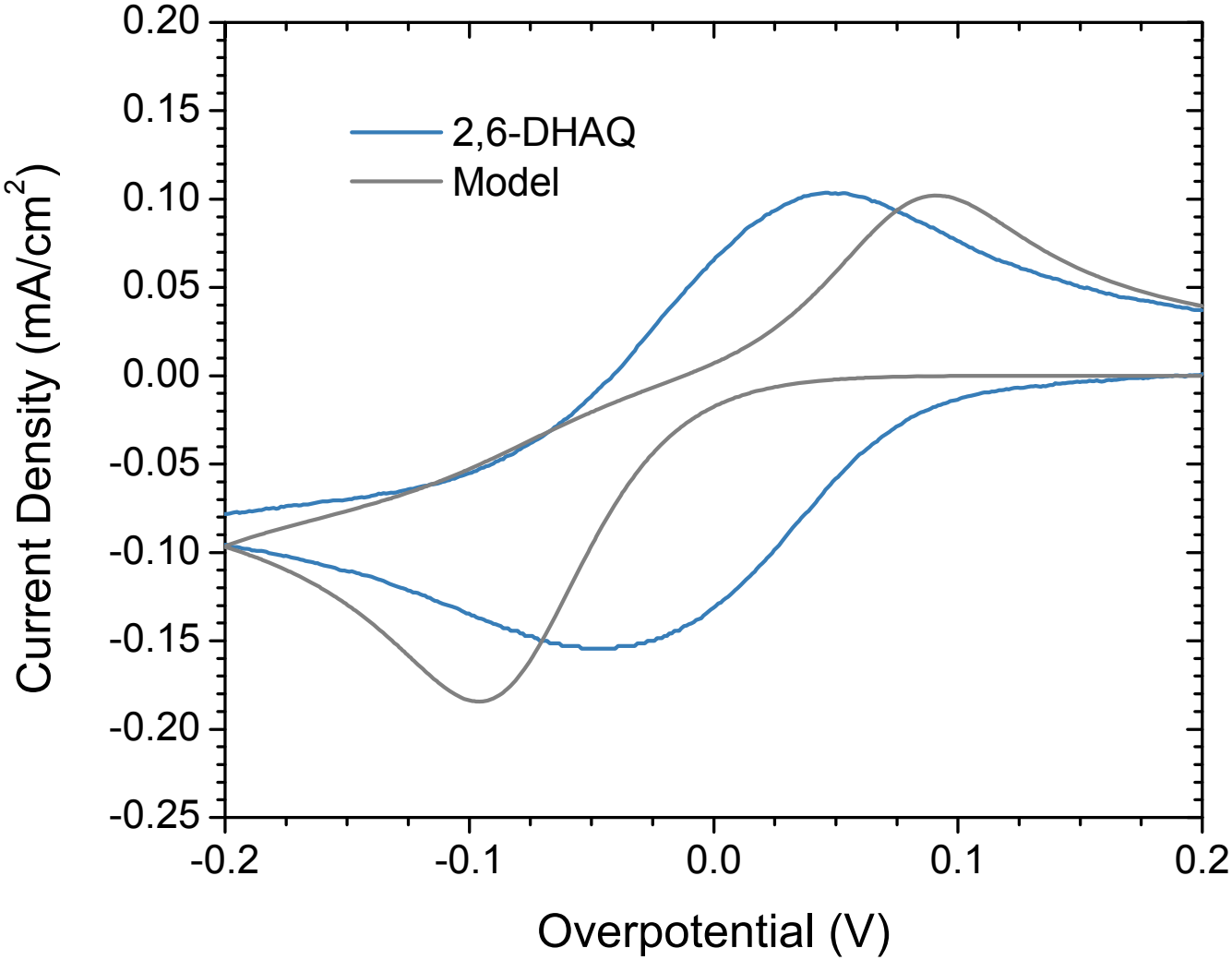
Two-electron transfer model can't explain CV



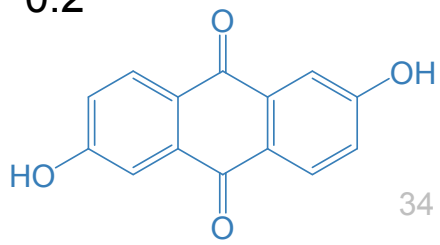
$k_0 = 1 \times 10^{-3}$ cm/s



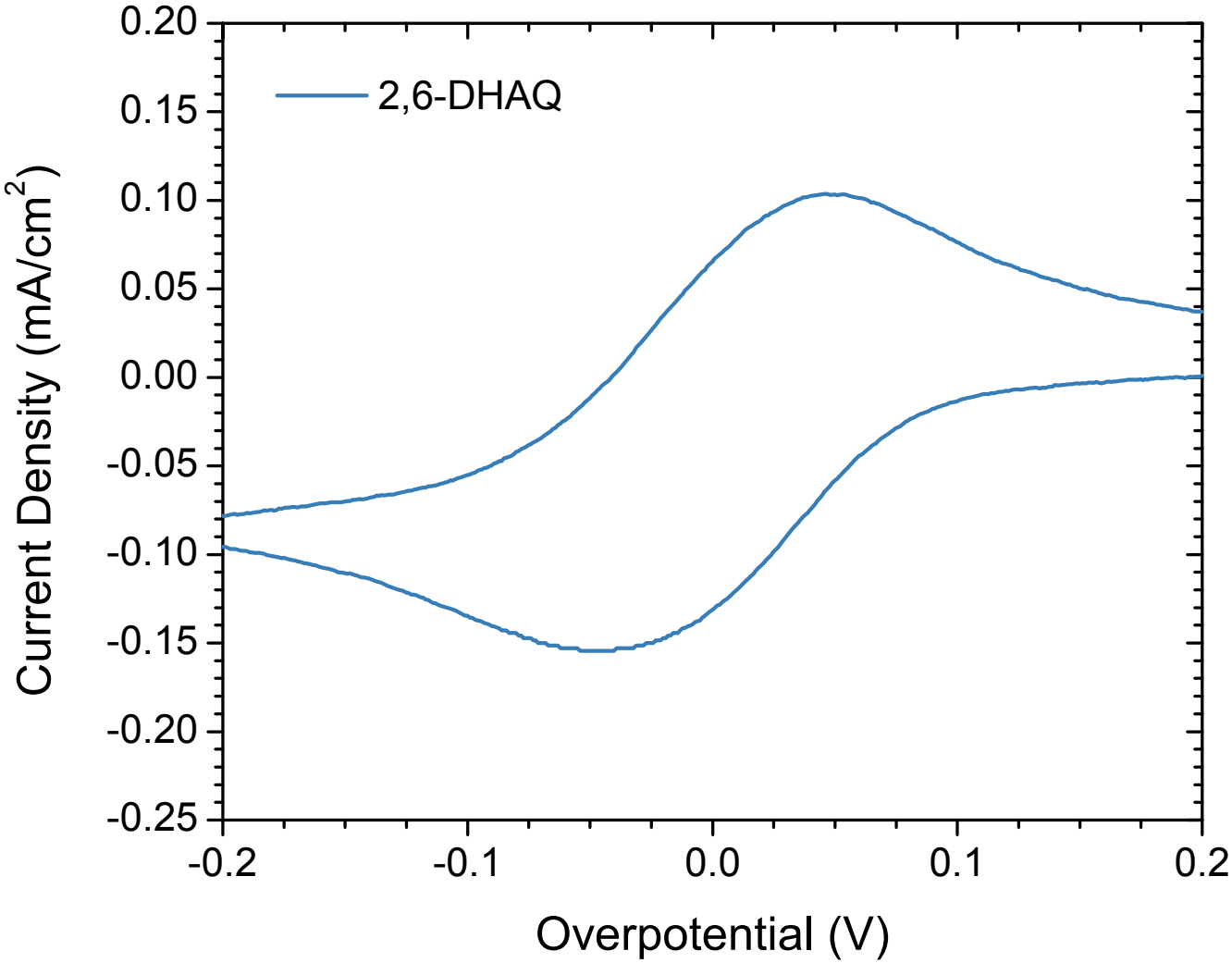
Two-electron transfer model can't explain CV

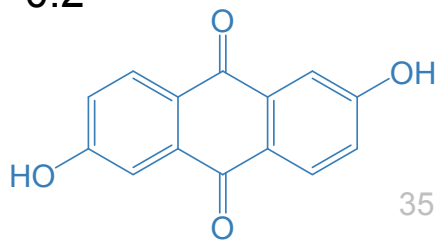


$k_0 = 1 \times 10^{-4}$ cm/s

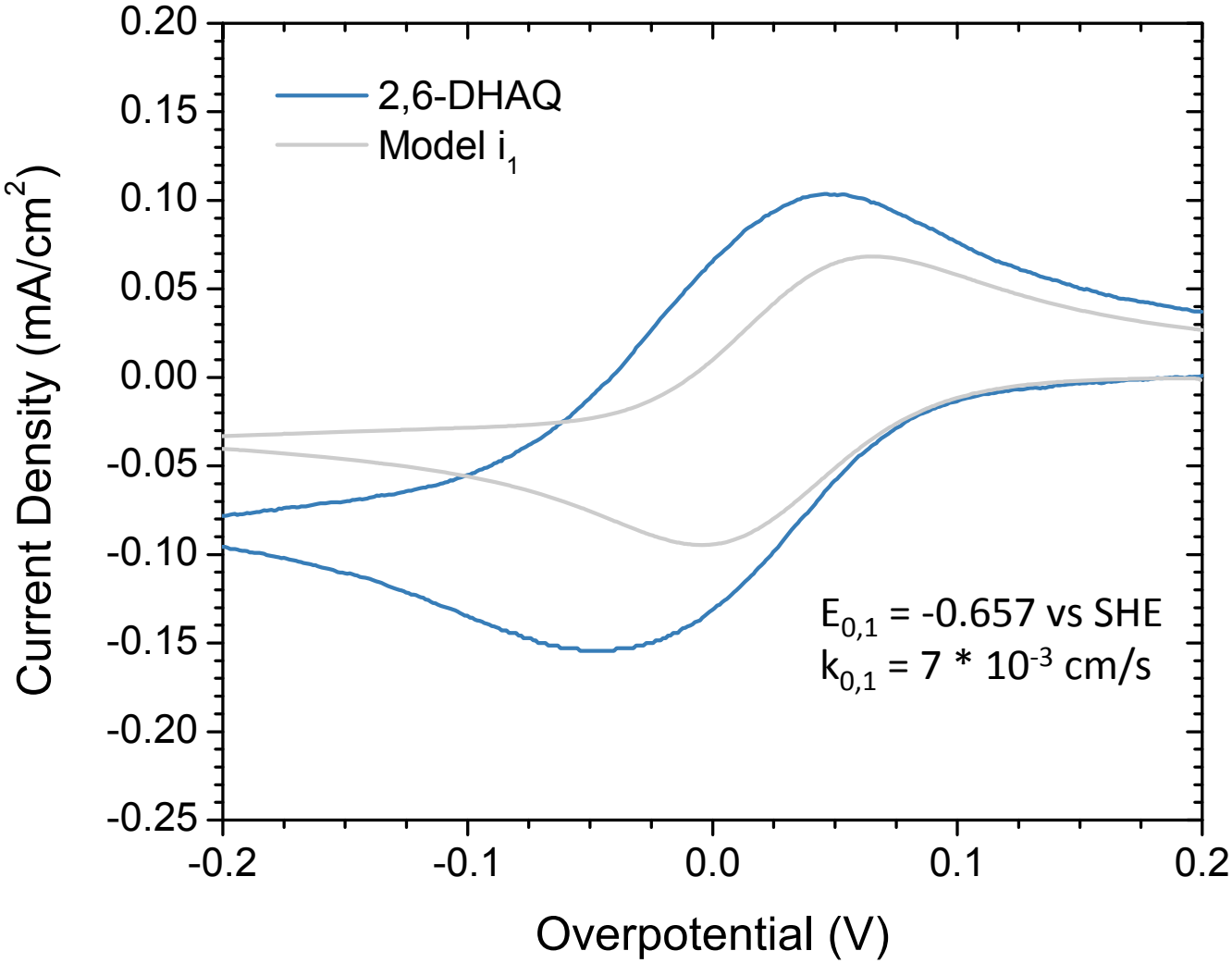


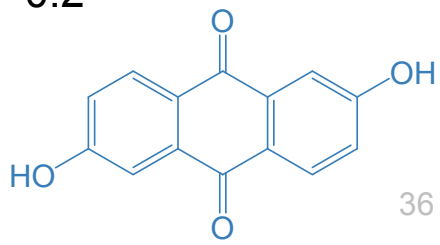
Sequential 1 e⁻ transfers could explain CV



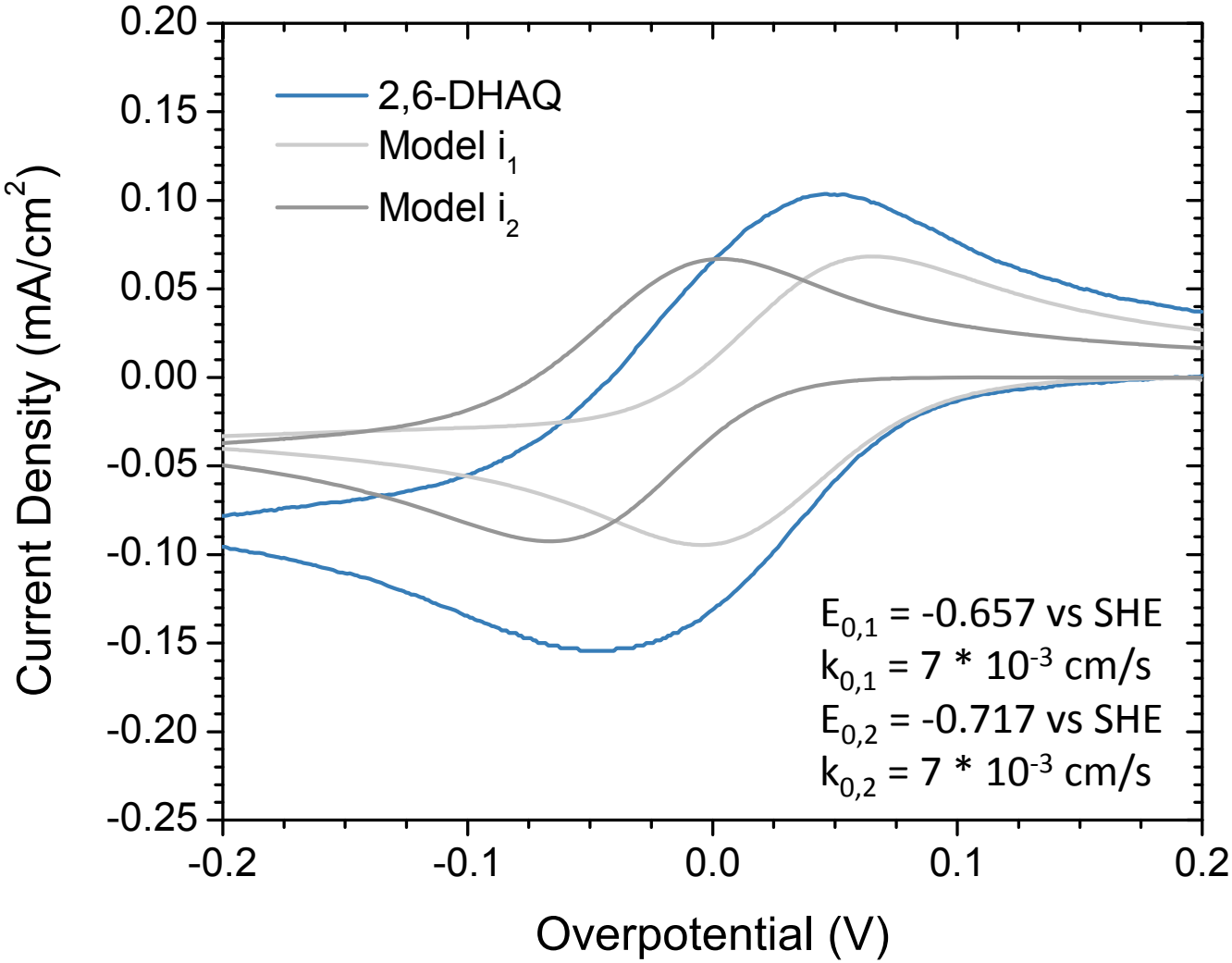


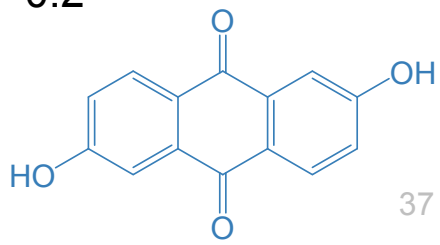
Sequential 1 e⁻ transfers could explain CV



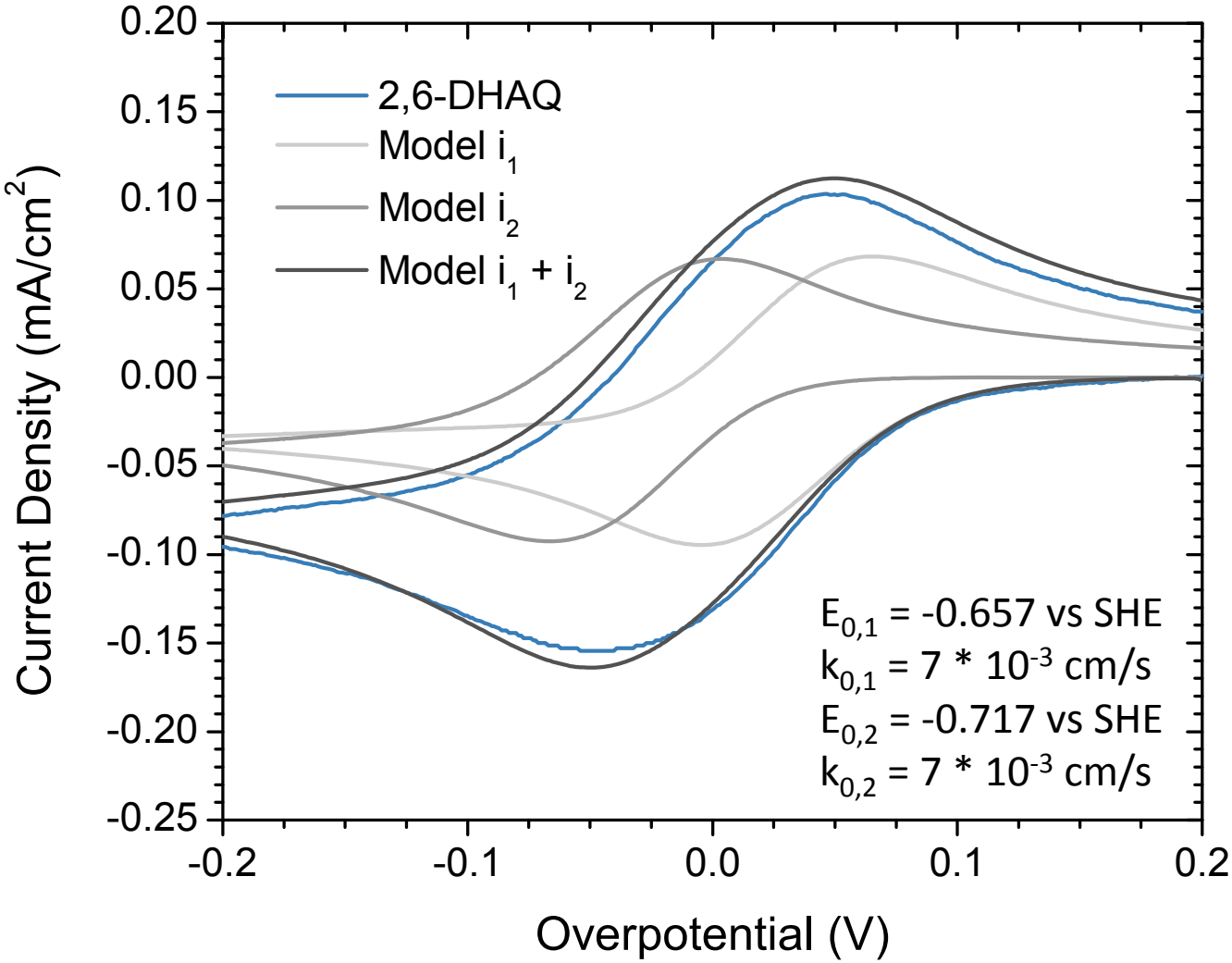


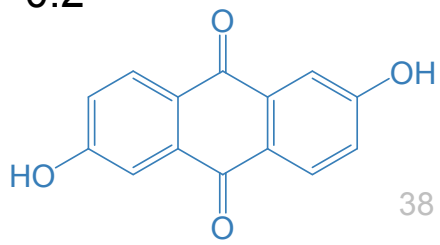
Sequential 1 e⁻ transfers could explain CV





Sequential 1 e⁻ transfers could explain CV





Quinone – Ferrocyanide Flow Battery

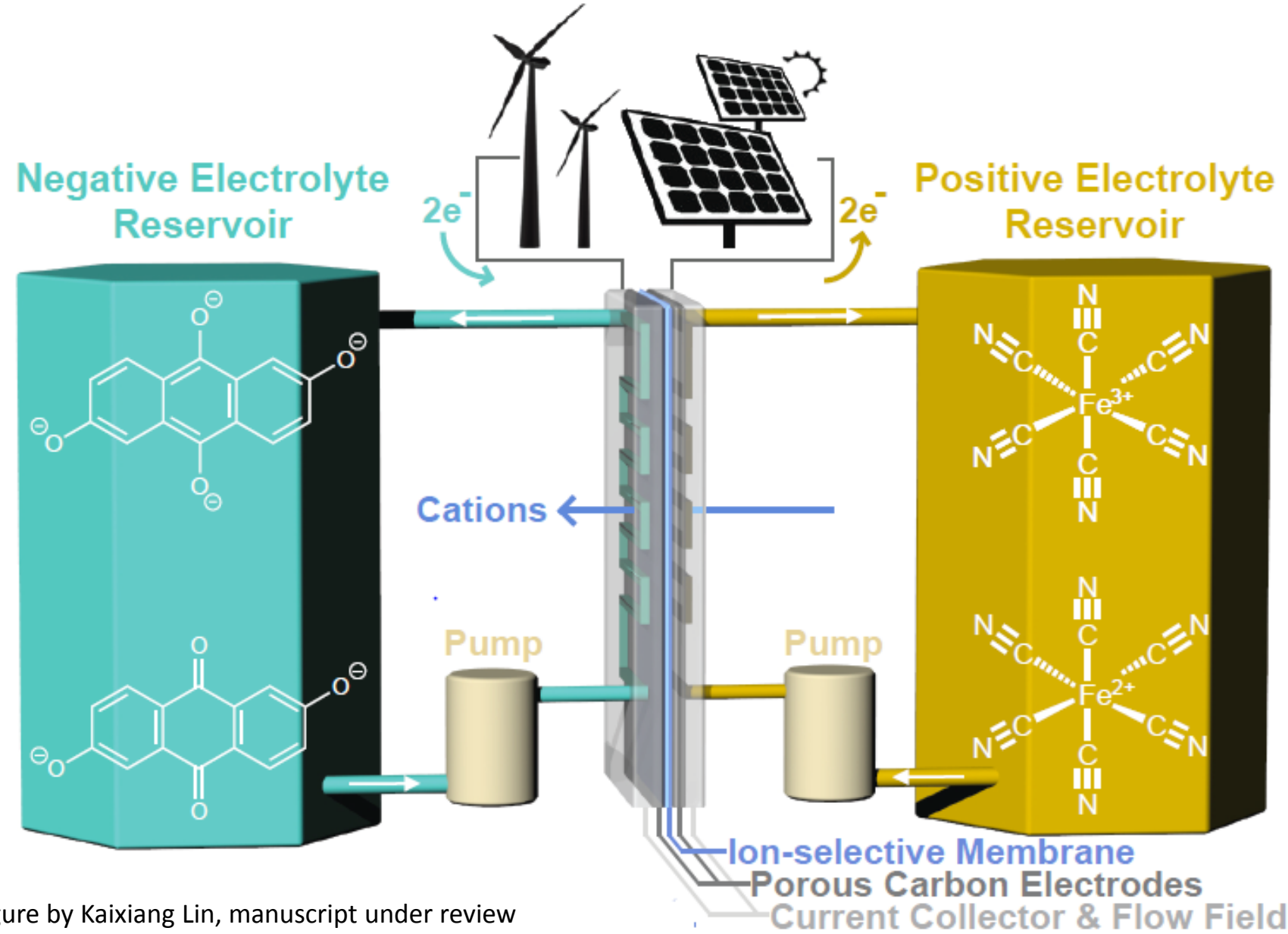
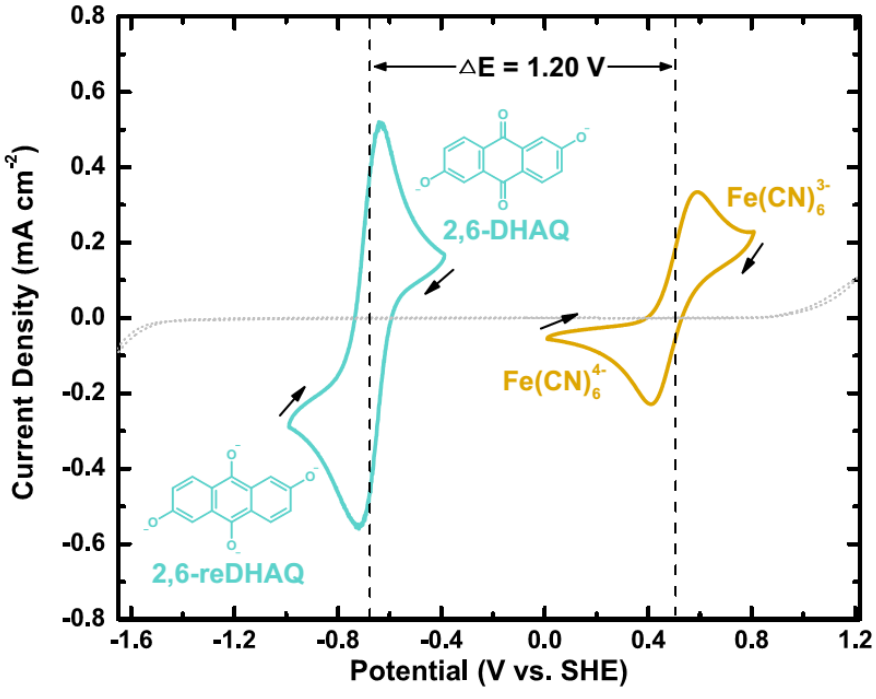
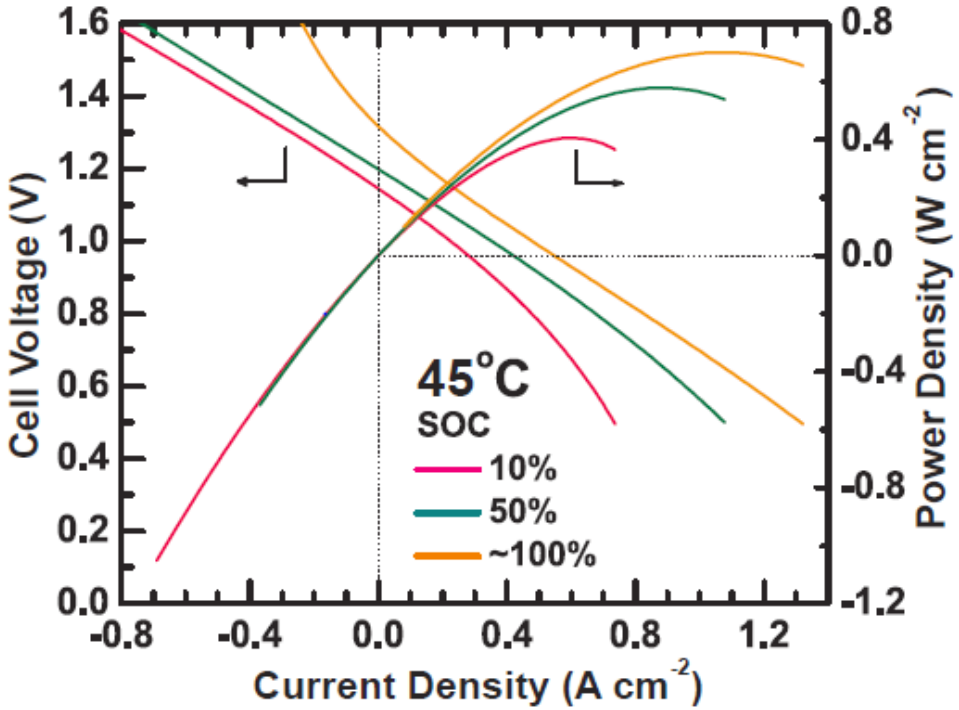


Figure by Kaixiang Lin, manuscript under review

Quinone – Ferrocyanide Flow Battery



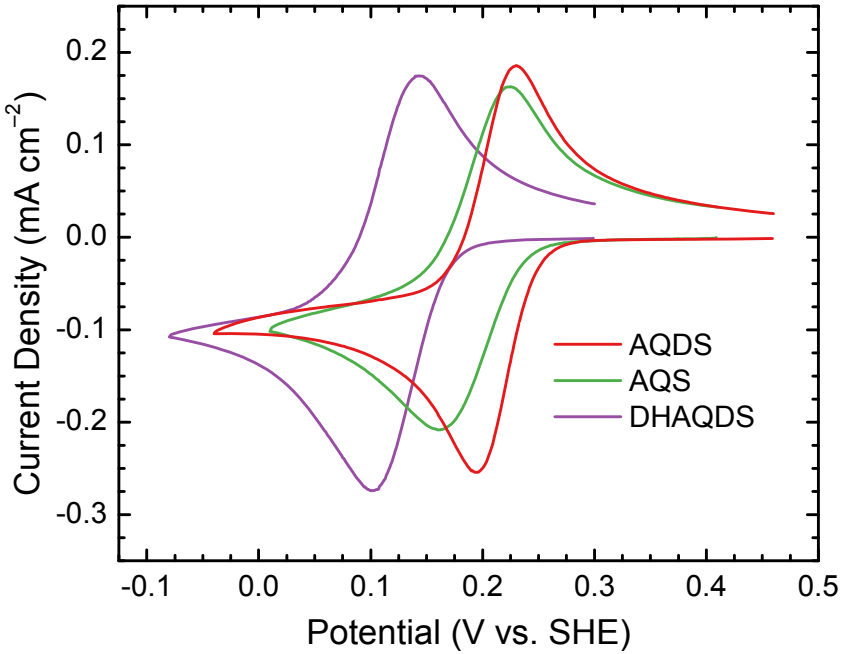


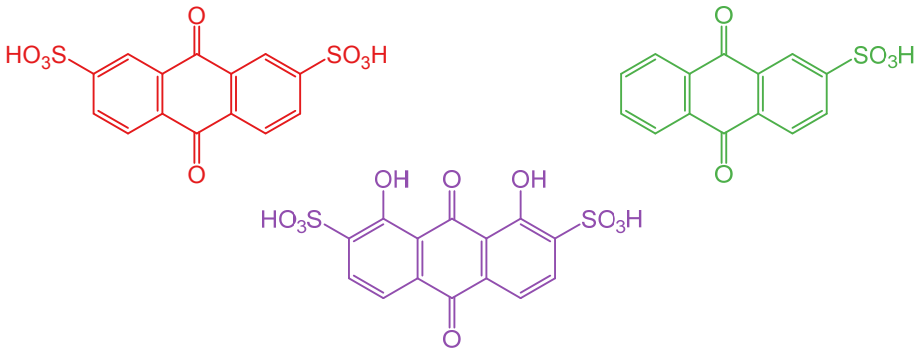
Cyclic voltammogram of 4 mM 2,6-DHAQ (dark cyan curve) and ferrocyanide (gold curve) scanned at 100 mV/s

Work performed by Kaixiang Lin, manuscript under review

Strategies for Increasing Cell Voltage

Use functional groups to create more reducing quinones





Strategies for Increasing Cell Voltage

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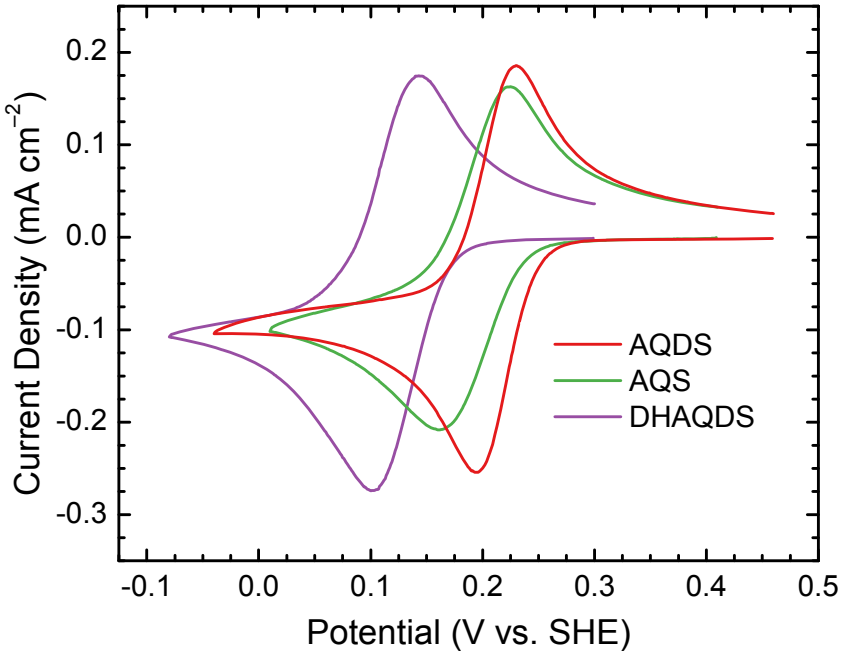
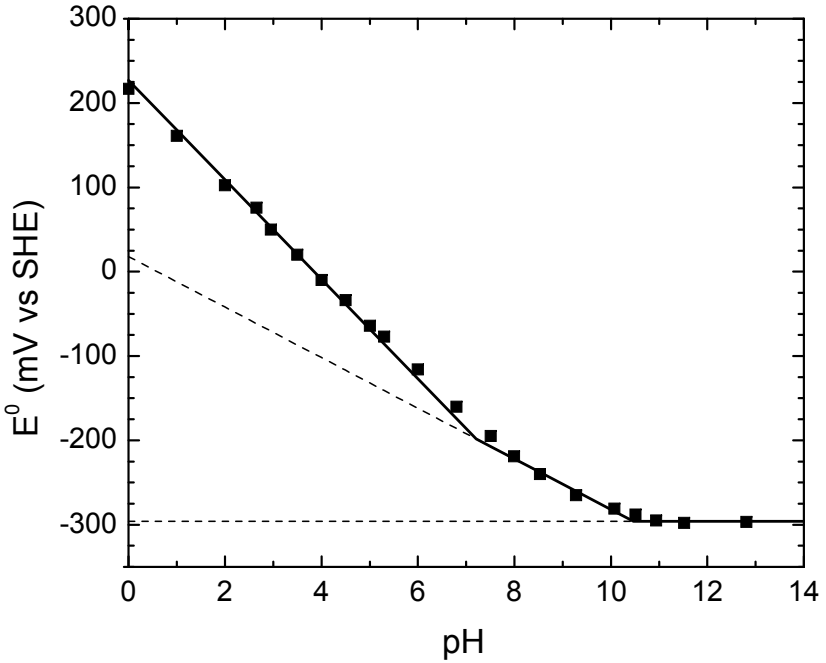
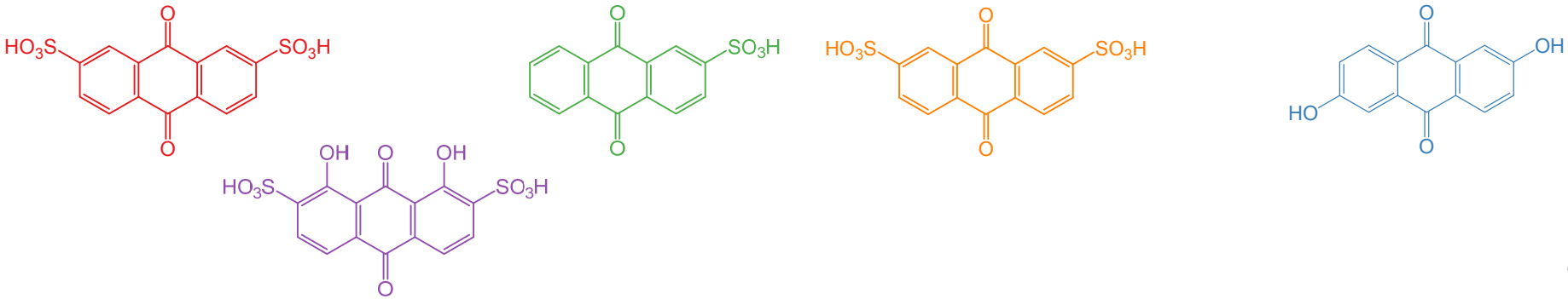


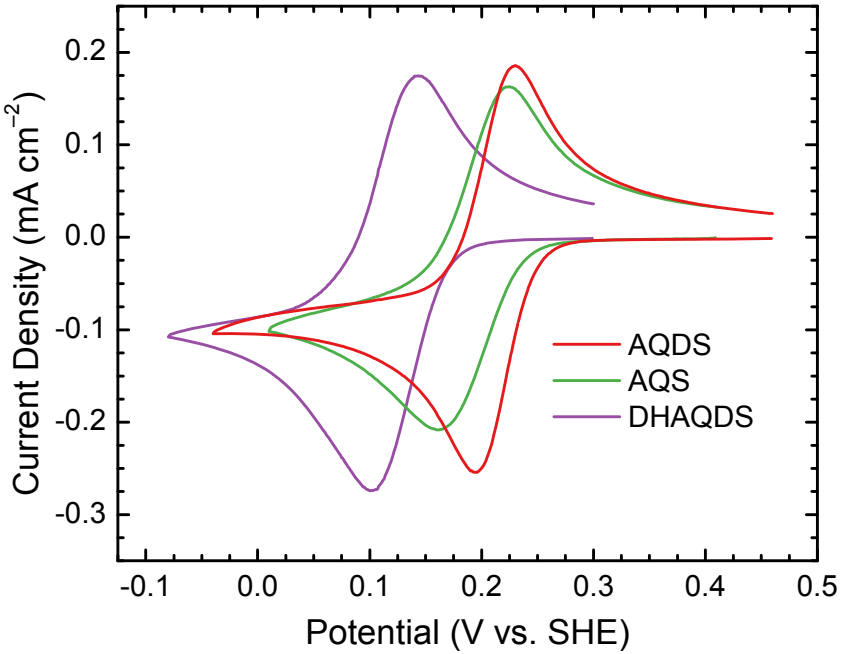
Use quinones in alkaline environment



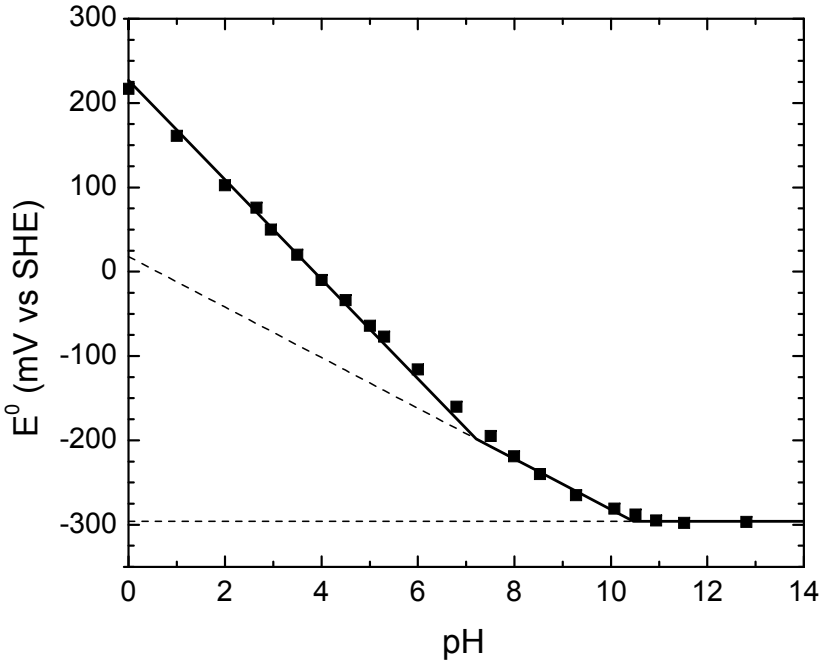


Strategies for Increasing Cell Voltage

Use functional groups to create more reducing quinones

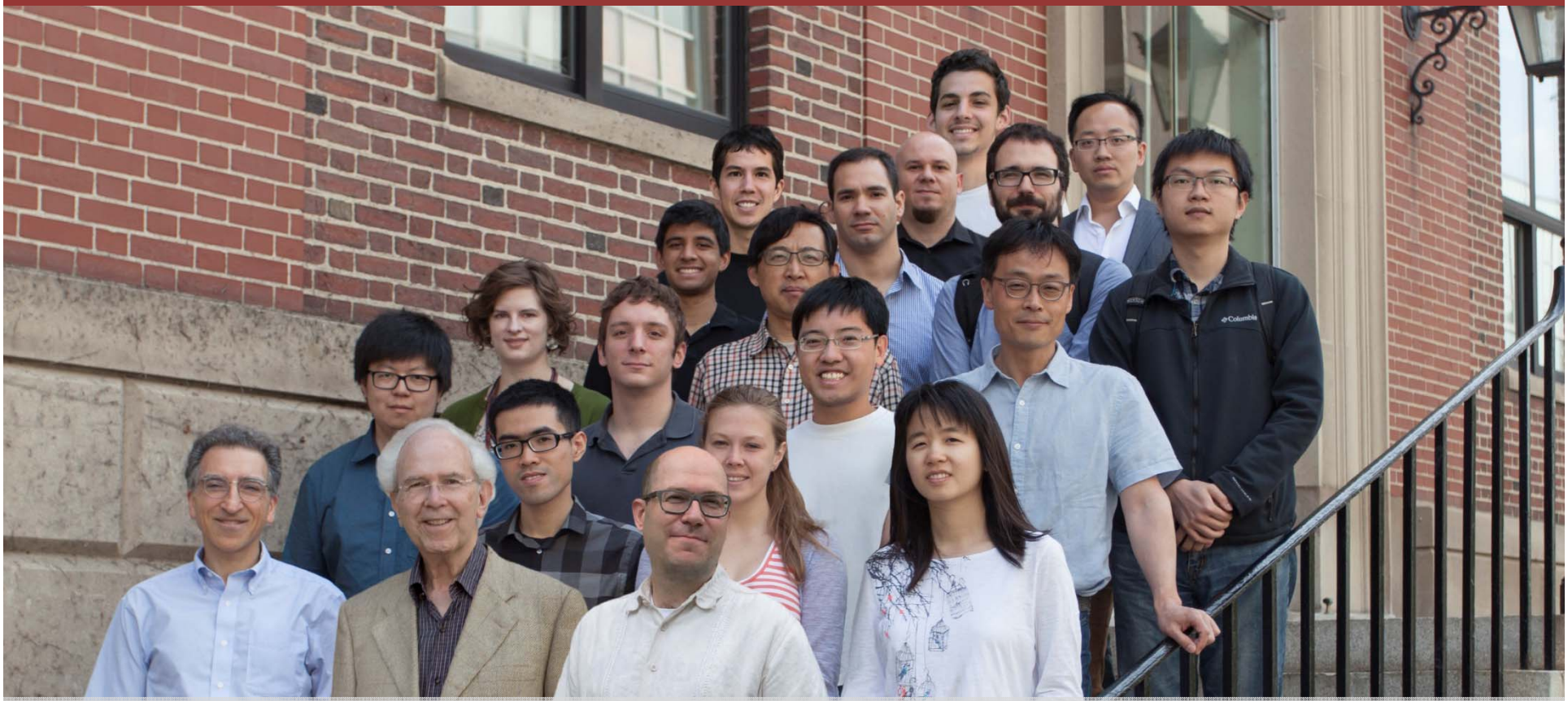


Use quinones in alkaline environment



ENFL 403: Organic Aqueous Redox Flow Batteries
Prof. Michael J. Aziz
Thursday, August 20, 1:35 pm Room 258B

Thank You



This work was partially funded through the US Department of Energy ARPA-E Award DE-AR0000348 and partially funded through the Harvard School of Engineering and Applied Sciences.

Top to bottom, left to right:

Drew Wong, Prof. Mauricio Salles, Alvaro Valle, Dr. Junling Huang

Dhruv Pillai, Prof. Michael Marshak, Dr. Rafa Gómez-Bombarelli, Liuchuan Tong

Lauren Hartle, Dr. Sungjin “James” Kim, Dr. Changwon Suh,

Kaixiang Lin, Michael Gerhardt, Dr. Eugene Beh

Dr. Qing Chen, Louise Eisenach, Jennifer Wei

Prof. Michael Aziz, Prof. Roy Gordon, Prof. Alán Aspuru-Guzik

Assumptions for reversible case

- Linear, planar diffusion
  - $\frac{\partial C_O(x,t)}{\partial t} = D_O \frac{\partial^2 C_O(x,t)}{\partial x^2}$
- Initial conditions:
  - $C_O(x, t = 0) = C_O{}^*, \quad C_R(x, t = 0) = 0$
- Boundary conditions:
  - $C_O(x \to \infty, t) = C_O{}^*$
- All current is diffusion controlled
  - $i(t) = nFAD_O \left(\frac{\partial C_O(x,t)}{\partial x}\right)_{x=0}$
- Reversible reaction. Nernst equation applies:
  - $\frac{C_O(x=0,t)}{C_R(x=0,t)} = e^{(E_i - vt - E^0)nF/RT}$

Notation follows Bard and Faulkner for the reaction O + ne → R.

Quasireversible Charge Transfer

- New boundary condition:

$$\frac{i(t)}{nFA} = D_O \left(\frac{\partial C_O(x,t)}{\partial x} \right)_{x=0} = k_f C_O(0,t) - k_b C_R(0,t)$$

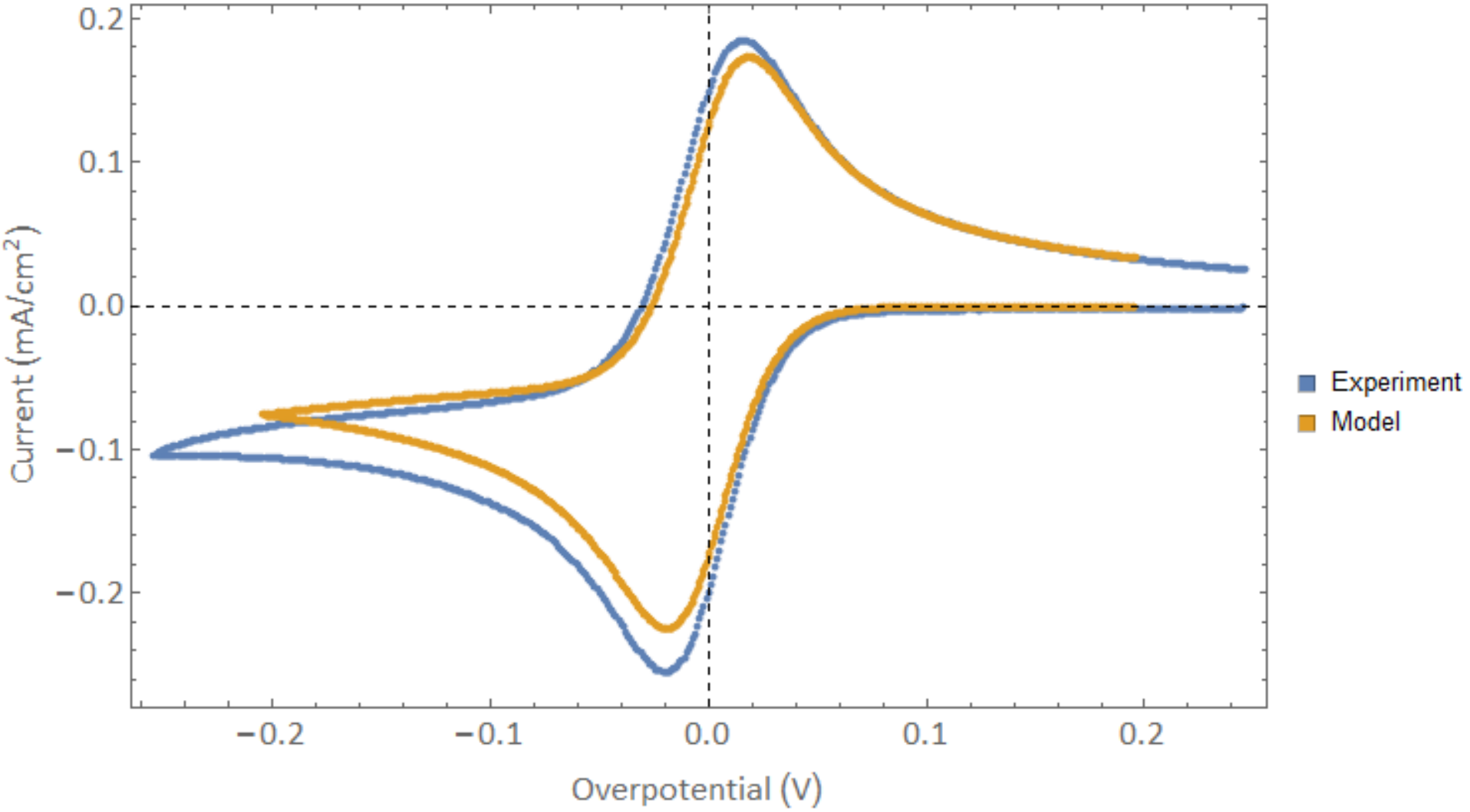
$$k_f = k_0 e^{\frac{-\alpha nF}{RT}(E-E^0)}, \qquad k_b = k_0 e^{\frac{(1-\alpha)nF}{RT}(E-E^0)}$$

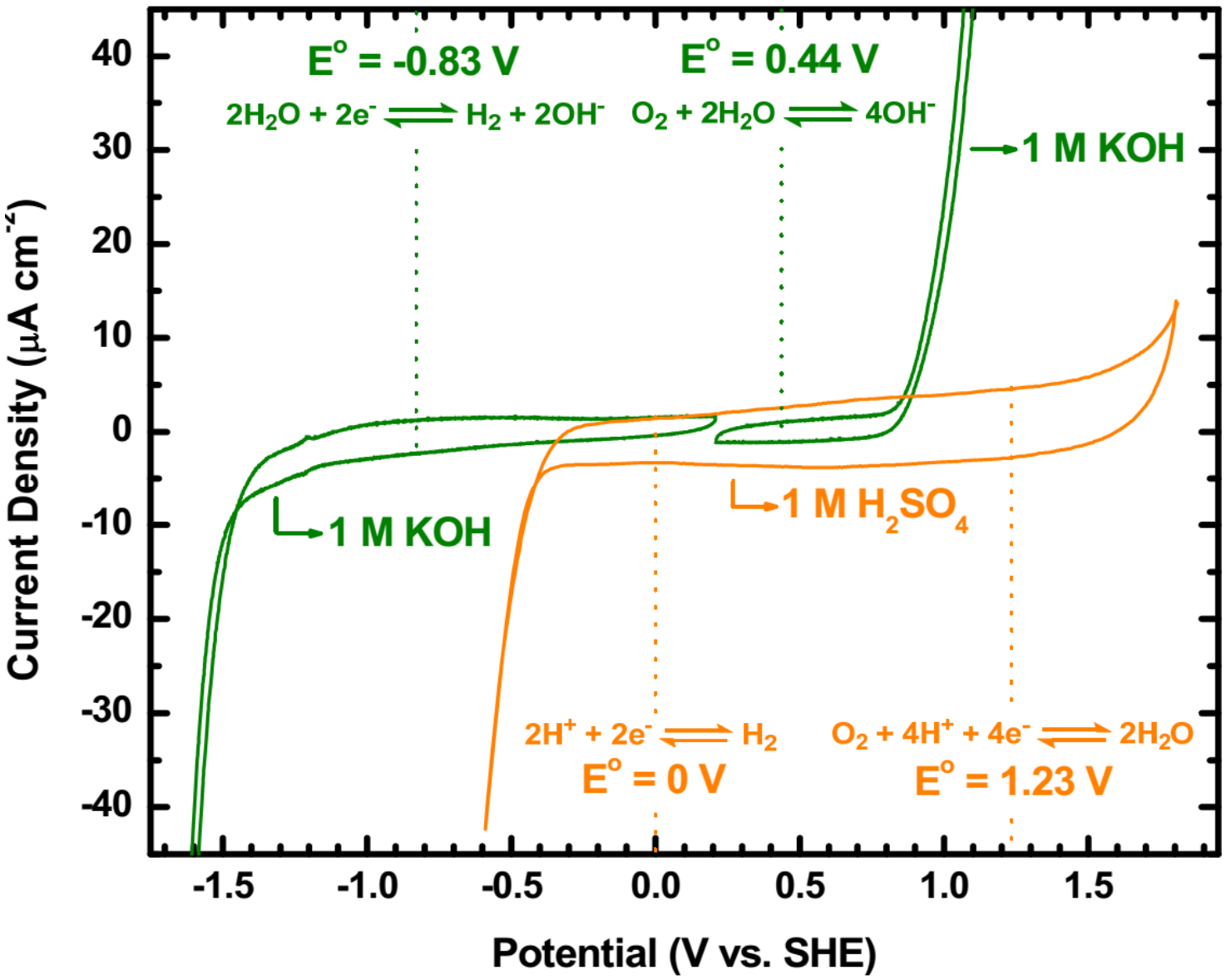
- Define a new variable: $\psi = \frac{\gamma^{\alpha} k_0}{\sqrt{\pi a D_O}}$ $\psi \to \infty$: Reversible; $\psi \to 0$: Irreversible

$$\frac{\chi(at)\left[\gamma(C_O^*/C_R^*)S(at)\right]^{\alpha}}{\psi} = 1 - S(at) - \int_0^{at} \frac{\chi(z)dz}{\sqrt{at-z}} - \gamma(C_O^*/C_R^*)S(at) \int_0^{at} \frac{\chi(z)dz}{\sqrt{at-z}}$$

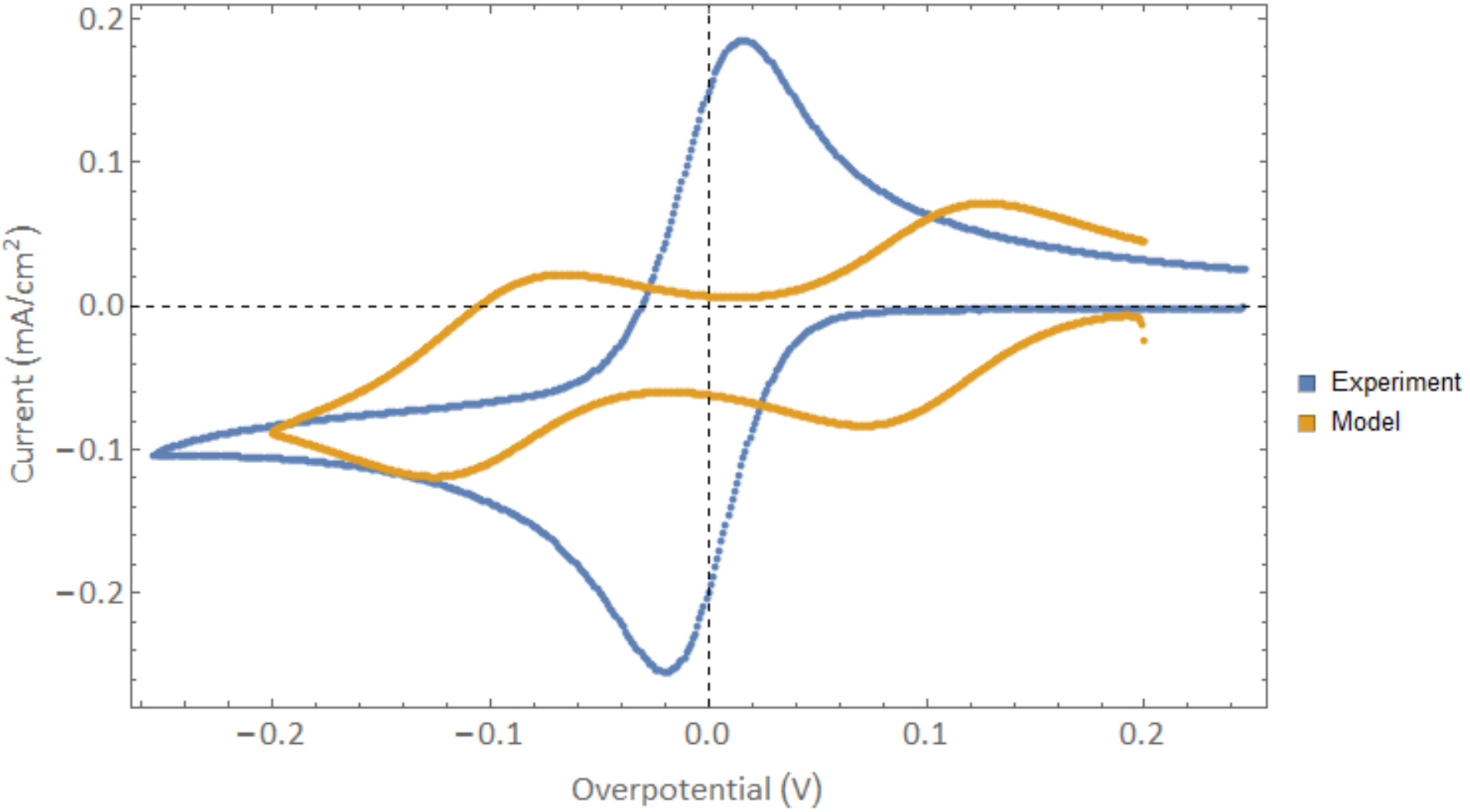
Nicholson, R. (1965). Theory and Application of Cyclic Voltammetry for Measurement of Electrode Reaction Kinetics. *Analytical Chemistry*, (21), 1351–1355. Retrieved from http://pubs.acs.org/doi/abs/10.1021/ac60230a016

AQDS redox assuming $k_0 = 7.2 \times 10^{-3}$




E° = -0.83 V
2H2O + 2e- ⇌ H2 + 2OH-
E° = 0.44 V
O2 + 2H2O ⇌ 4OH-
1 M KOH
1 M KOH
1 M H2SO4
2H+ + 2e- ⇌ H2
E° = 0 V
O2 + 4H+ + 4e- ⇌ 2H2O
E° = 1.23 V
Current Density (μA cm-2)
Potential (V vs. SHE)
40
30
20
10
0
-10
-20
-30
-40
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5

The 1+1 model fails to explain AQDS redox



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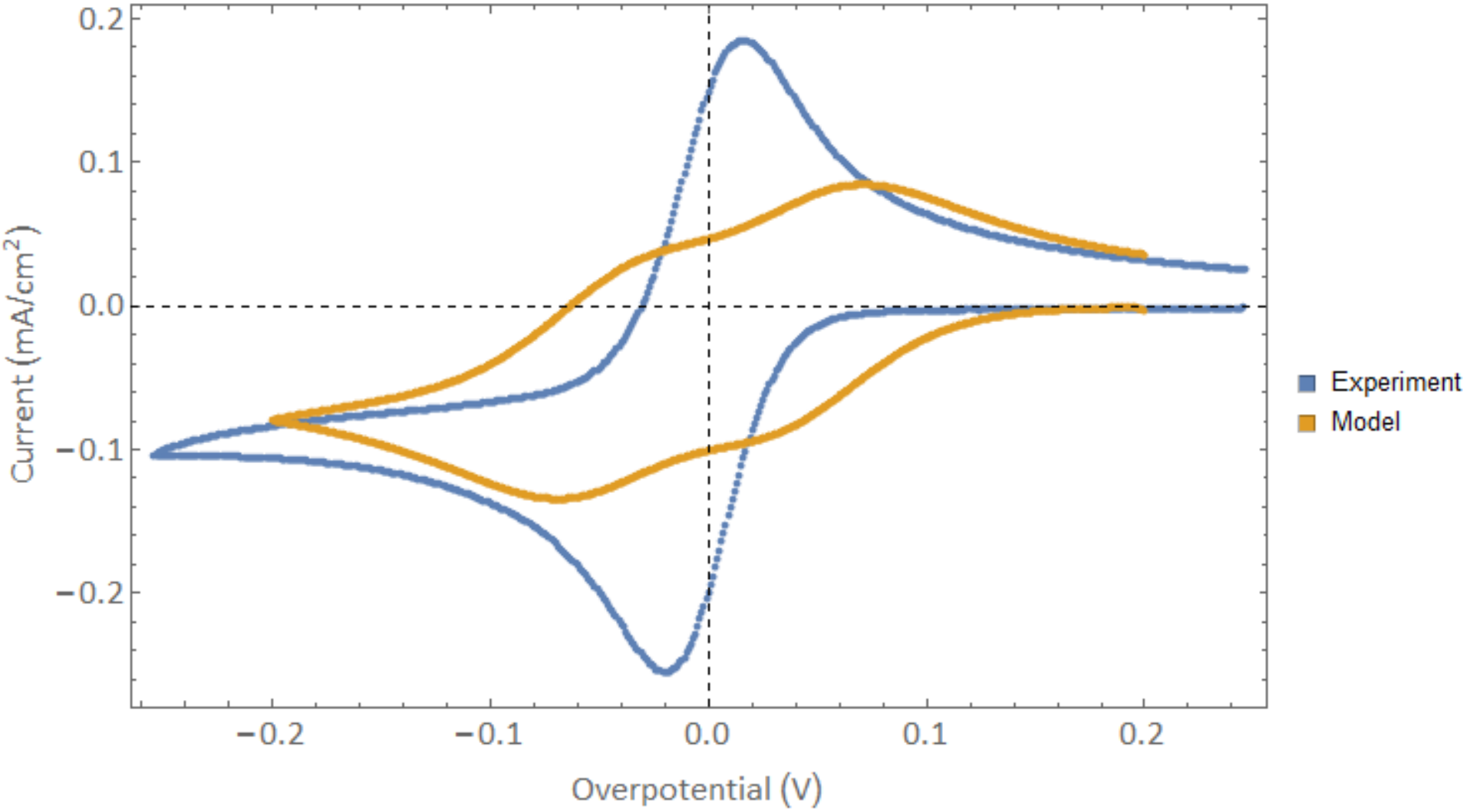

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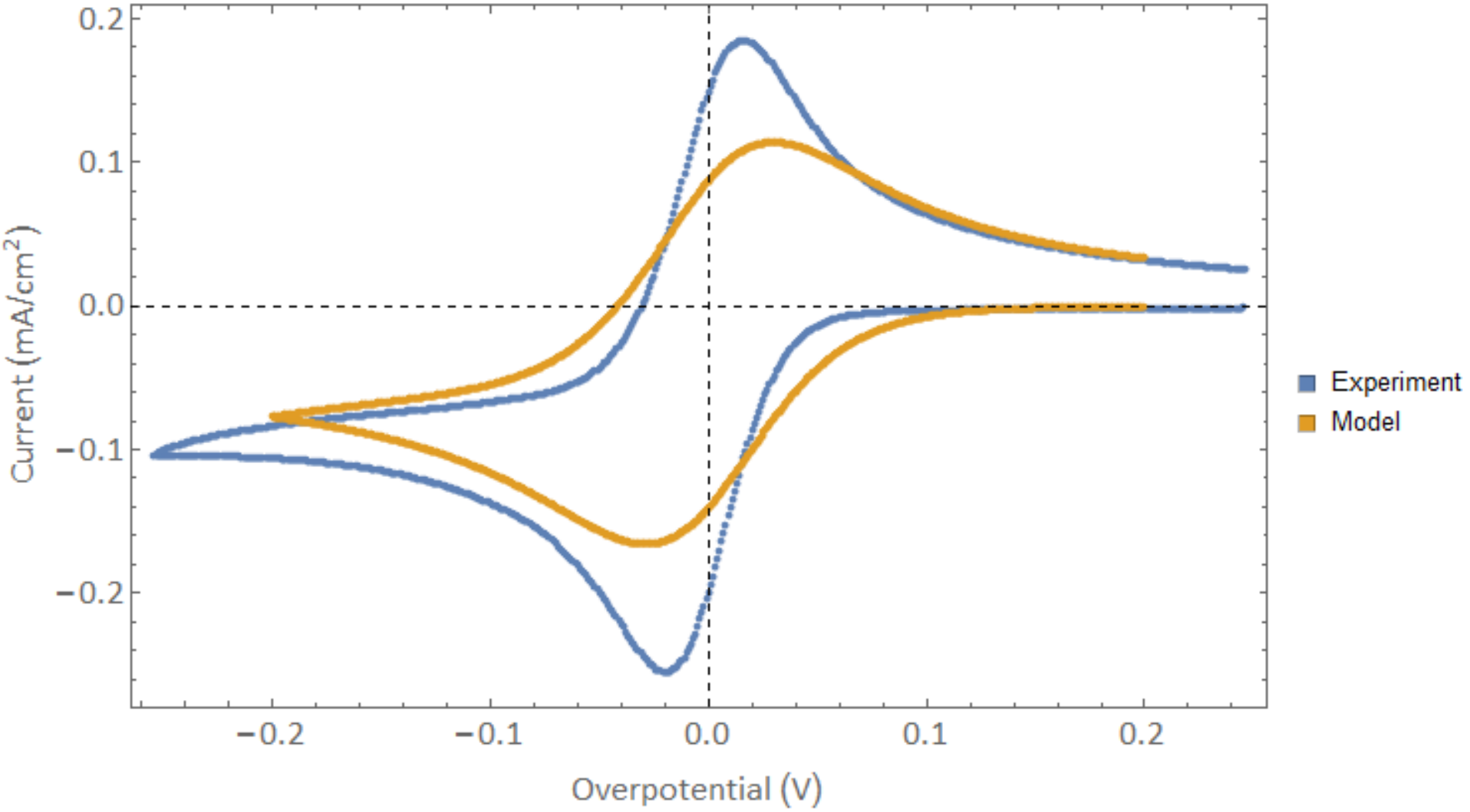
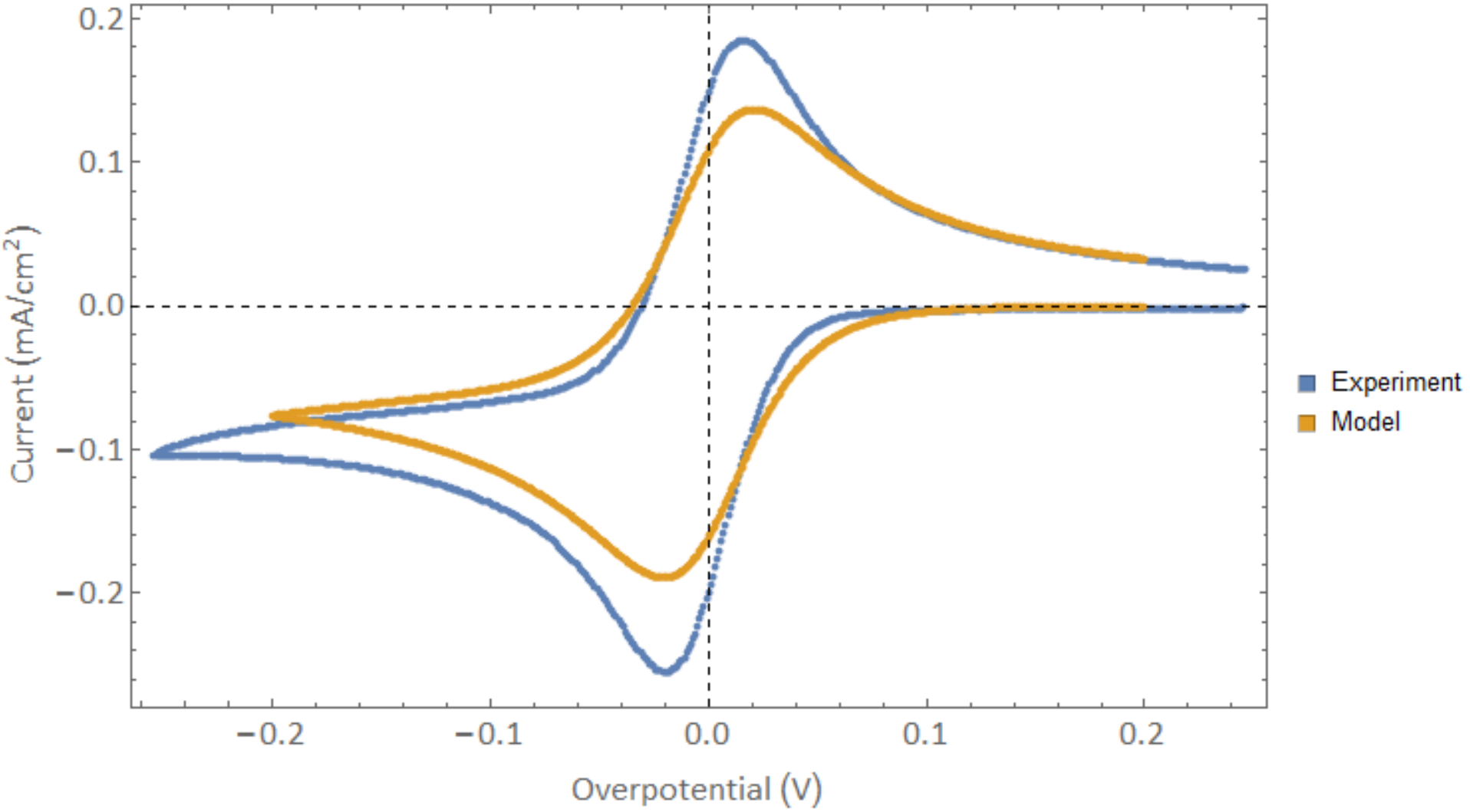
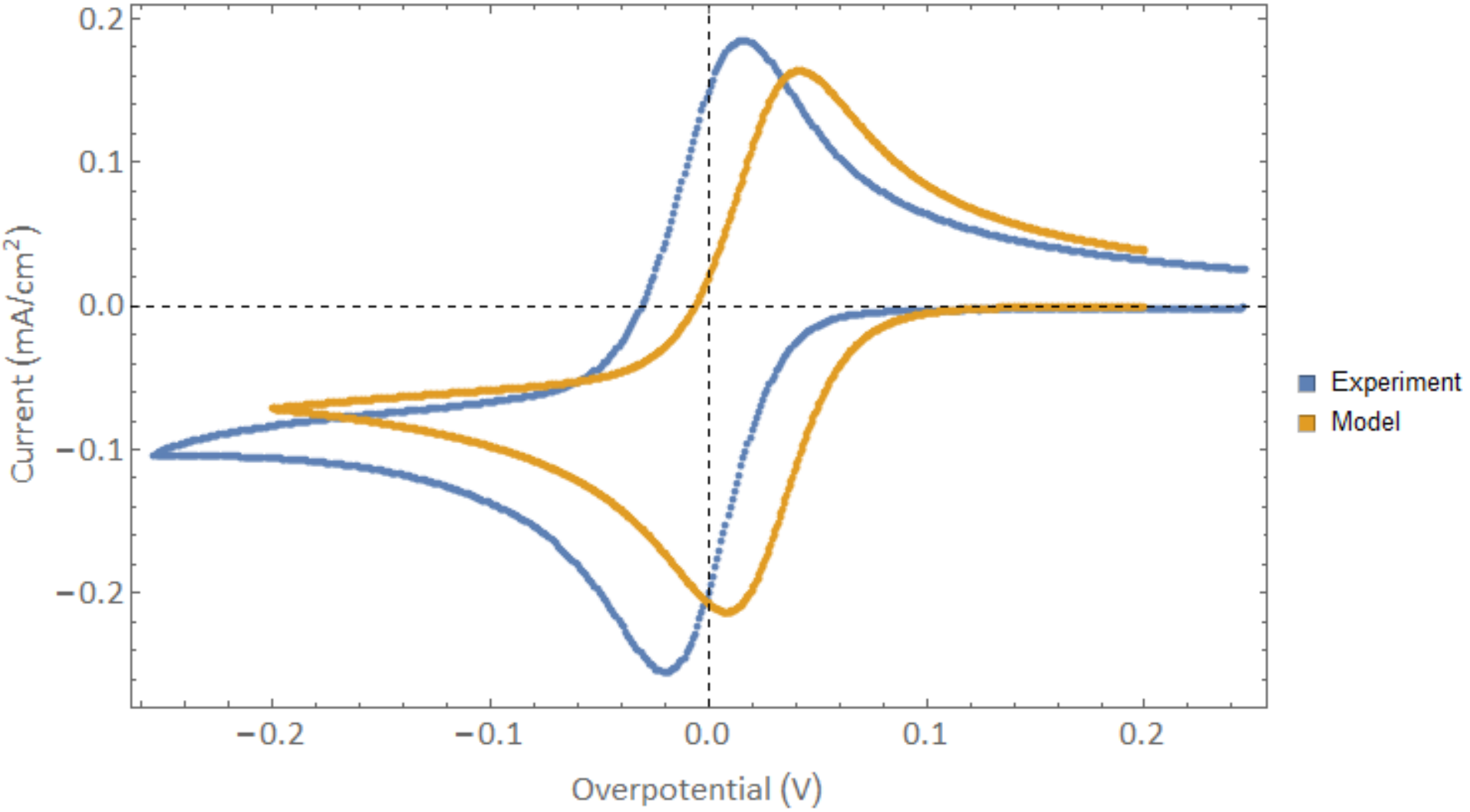


The 1+1 model fails to explain AQDS redox



The 1+1 model fails to explain AQDS redox



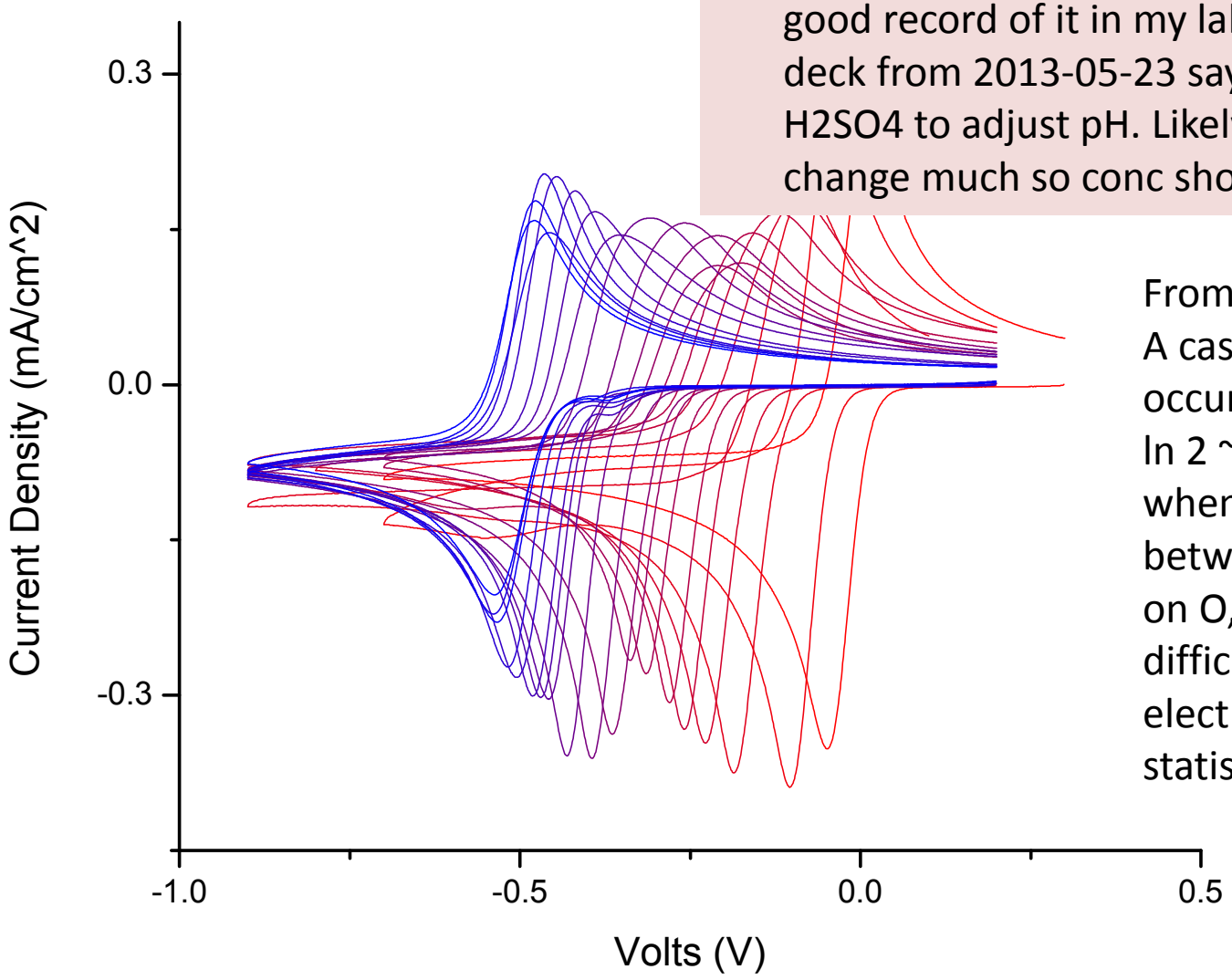
Abstract text

Aqueous quinone/hydroquinone couples exhibit rapid redox kinetics, require no electrocatalyst, and are inexpensive, making them attractive candidates for large-scale energy storage devices such as flow batteries [1–3]. In acidic solutions, quinones undergo a rapid two-proton, two-electron reduction; however, in alkaline aqueous solutions, the picture is less clear[4]. Under the right conditions, a two-electron reduction can occur as successive one-electron steps separated by a small difference in the reduction potential of each step. The underlying mechanism for the reduction of various quinones is explored as a function of pH and reduction potential. Using substituted anthraquinones and the bromine/hydrobromic acid couple, a flow battery exhibiting an open circuit voltage above 1.0 V and a peak galvanic power density above 0.7 W cm^{-2} is demonstrated. Furthermore, by employing soluble metal coordination complexes, a flow battery with an open circuit voltage exceeding 1.3 V is demonstrated. Mechanisms of capacity loss during cell cycling are discussed.

(1) Huskinson, B.; Marshak, M. P.; Suh, C.; Er, S.; Gerhardt, M. R.; Galvin, C. J.; Chen, X.; Aspuru-Guzik, A.; Gordon, R. G.; Aziz, M. J. *Nature* **2014**, *505* (7482), 195.
(2) Huskinson, B.; Marshak, M.; Gerhardt, M.; Aziz, M. *ECS Trans.* **2014**, *61* (37), 27.
(3) Yang, B.; Hoober-Burkhardt, L.; Wang, F.; Surya Prakash, G. K.; Narayanan, S. R. *J. Electrochem. Soc.***2014**, *161* (9), A1371.
(4) Quan, M.; Sanchez, D.; Wasylkiw, M. F.; Smith, D. K. *J. Am. Chem. Soc.* **2007**, *129* (42), 12847.

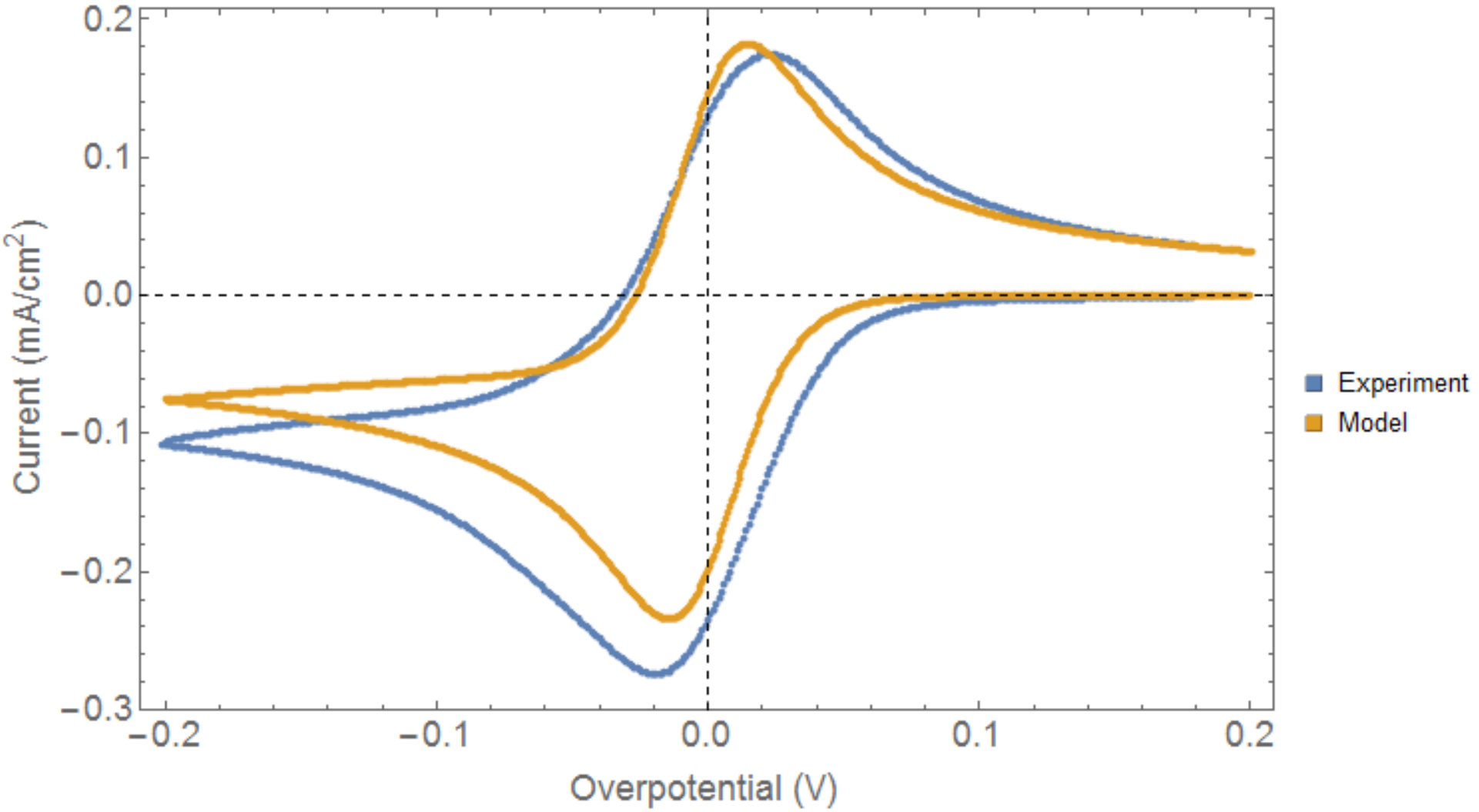
Check out 2013-04-xx thru 2013-06-xx
In Half Cell Electrochemistry
Also the Pourbaix diagram origin file

1. Is concentration constant?
   I think it's a fair assumption to make. I don't explicitly say it is anywhere and I don't have a good record of it in my lab notebook. But my slide deck from 2013-05-23 says I was adding KOH and H2SO4 to adjust pH. Likely the volume didn't change much so conc shouldn't change much.



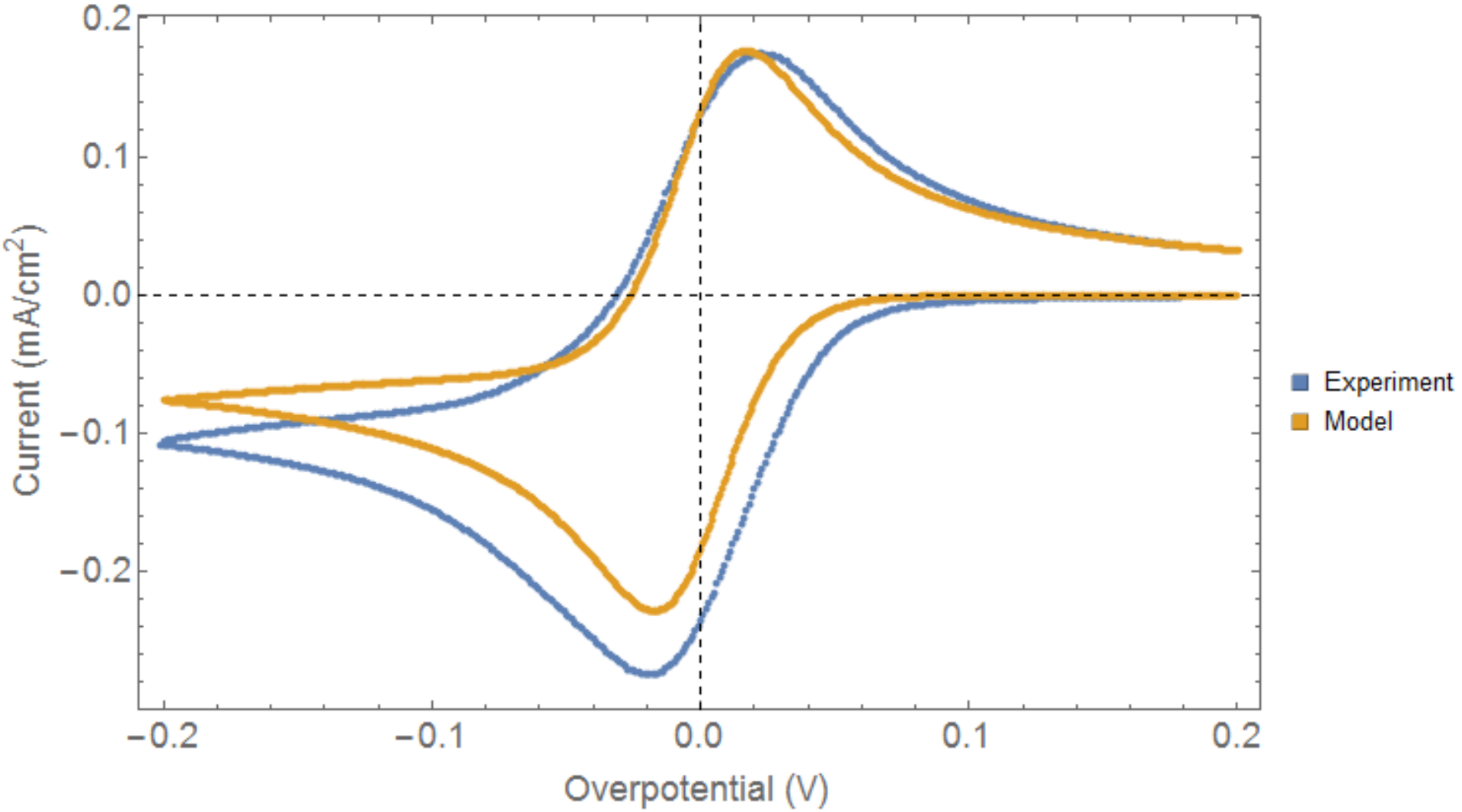
From Bard:
A case of particular interest occurs when deltaE0 = -2RT/F ln 2 ~ -35.6 mV. This occurs when there is no interaction between the reducible groups on O, and the additional difficulty adding the extra electron arises purely from statistical (entropic) factors.

DHAQDS redox is less clear



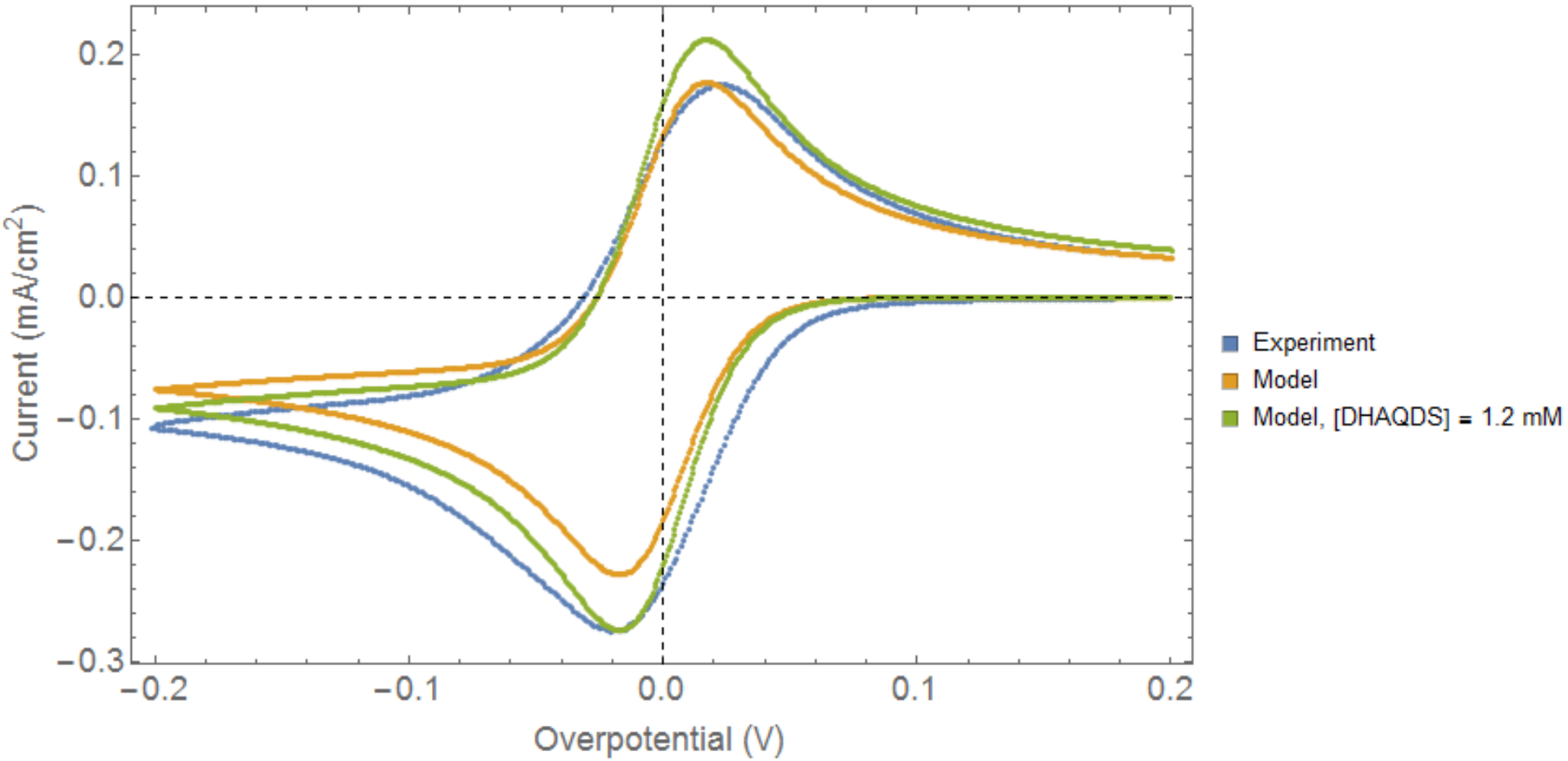
Reversible model doesn't quite fit

DHAQDS redox is less clear



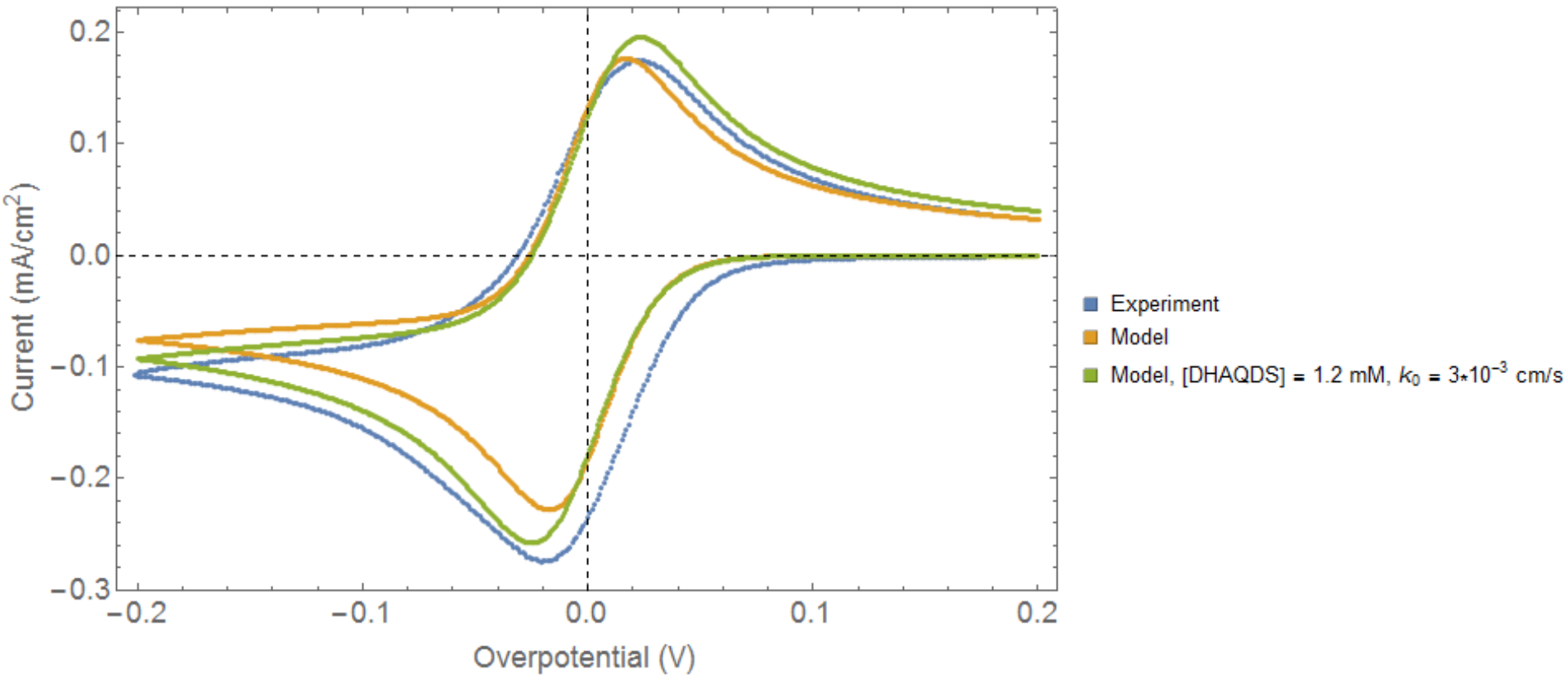
Plugging in measured k0 value helps a little

DHAQDS redox is less clear



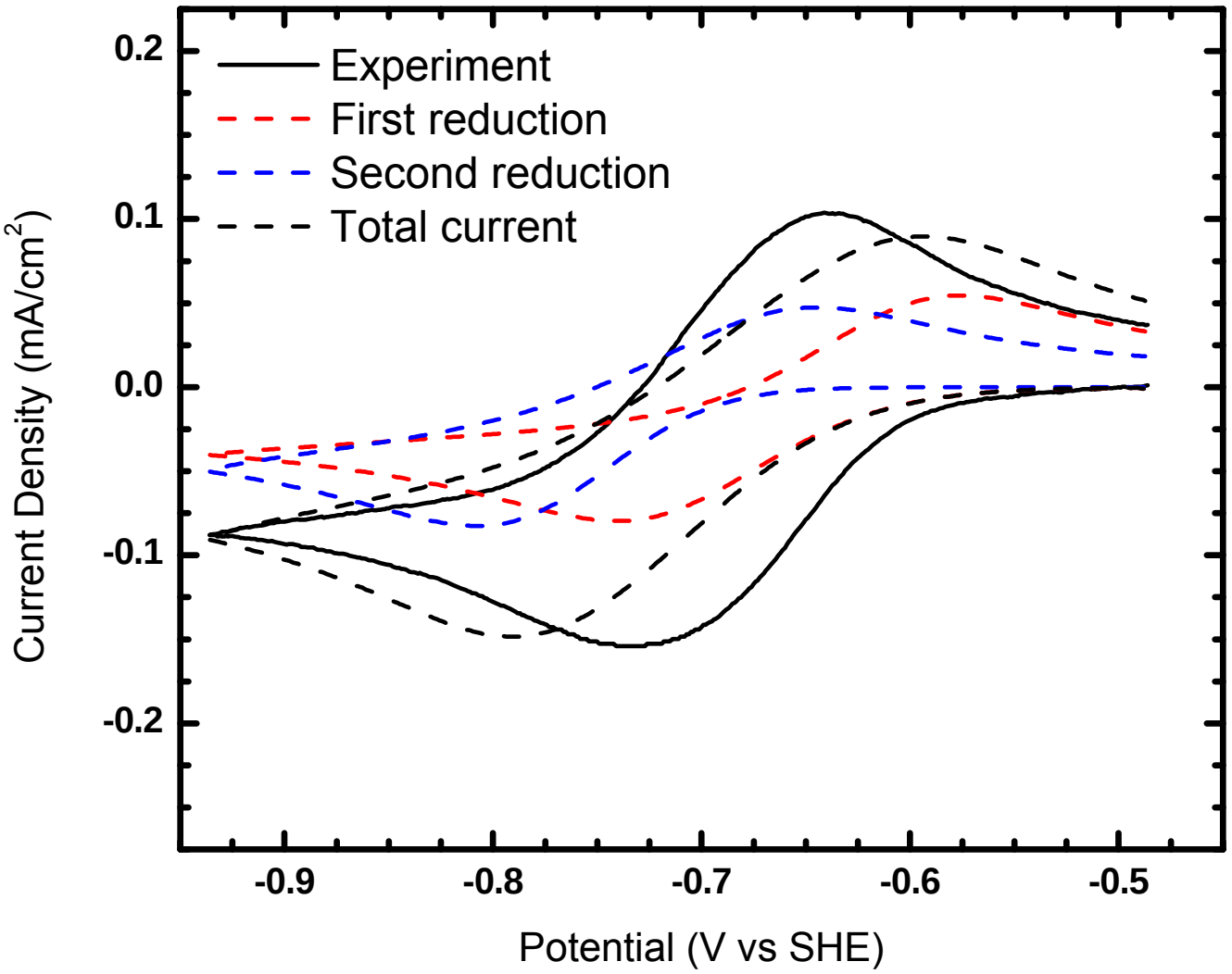
Assuming a higher bulk DHAQDS concentration explains the height of the reduction peak

DHAQDS redox is less clear



Assuming more sluggish kinetics on top of concentration error doesn't explain it

Setting a lower bound on k_0 for 2,6-DHAQ



$E_{0,1}$ = -0.657 vs SHE
$k_{0,1}$ = 7 * 10^{-4} cm/s
$E_{0,2}$ = -0.717 vs SHE
$k_{0,2}$ = 7 * 10^{-4} cm/s

Sequential 1 e⁻ transfers could explain CV